Studies of the complexation behaviour of transition metals applicable in membrane technologies

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a	aqueous
A	membrane area (m^2)
bl	boundary layer
BLM	Bulk Liquid Membranes
c_{HL}	analytical concentration of monomeric ligand ($g.m^{-3}$)
$c_{M^{n+}}$	analytical concentration of metal ion ($g.m^{-3}$)
CLM	Contained Liquid Membranes
D	Diffusion coefficient ($m^2.h^{-1}$)
D_{bl}	Diffusion coefficient of metal ions through boundary layer ($m^2.h^{-1}$)
D_m	Diffusion coefficient of metal ions through membrane phase ($m^2.h^{-1}$)
D.P.	direct procedure
ELM	Emulsion Liquid Membranes
FLM	Flowing Liquid Membrane
FT-IR	Fourier-Transform Infrared spectroscopy
HL	acidic carrier molecule (monomeric)
$(HL)_2$	dimeric ligand molecule
HSAB	Hard-Soft Acid-Base principle
i	interfacial
ID	inner diameter (µm)
ILM	Immobilized Liquid Membrane
J	flux ($g.m^{-2}.h^{-1}$)
J_{bl}	flux of metal ions through boundary layer ($g.m^{-2}.h^{-1}$)
J_m	flux of metal ions through membrane phase ($g.m^{-2}.h^{-1}$)
$k_{M^{n+}}$	distribution coefficient of the metal ion
l	membrane thickness (m)
K	equilibrium constant
m	degree of complex solvatation with neutral extractant molecules
$[M^{n+}]_a$	metal concentration in aqueous phase ($g.m^{-3}$)
MINA	Flemish Environmental Policy plan
MIRA	Flemish Environmental Report
ML_n	metal complex

M^{n+}	metal ion
n	number of extractant molecules in the complex
$\overset{0}{n}_{M^{n+}}$	overall molar flow ($g.h^{-1}$)
$\overset{0}{n}_{M^{n+},bl}$	molar flow of metal ions through boundary layer ($g.h^{-1}$)
$\overset{0}{n}_{M^{n+},m}$	molar flow of metal ions through membrane phase ($g.h^{-1}$)
o	organic
OD	outer diameter (µm)
p	degree of complex polymerization
P	permeability ($m.h^{-1}$)
PARCOM	Paris Commission
P_c	critical displacement pressure ($N.m^{-2}$)
$pH_{0.5}$	pH of 50% metal extraction
PIM	Polymer Inclusion Membrane
pK_a	acid dissociation constant
%E	extraction percentage
r	pore radius (m)
R	alkyl chain
S	sugar type
SLM	Supported Liquid Membrane
t	time (h)
T_g	glass transition temperature
TOC	Total Organic Carbon
UV-VIS	ultraviolet-visible
V	volume (m^3)
x	thickness (m)
$x_{M^{n+}}$	mole-fraction of metal ion
x_{max}	maximum of continuous variation plot
$\frac{\partial c}{\partial x}$	concentration gradient ($g.m^{-4}$)

Greek letters

δ_{bl}	thickness of boundary layer (m)
ε	absorptivity
γ	interfacial tension between strip or feed solution and the liquid membrane phase ($N.m^{-1}$)
μ	viscosity (Pa.s)
ν	frequency (cm^{-1})
θ	contact angle
ρ	density ($kg.m^{-3}$)
σ	surface tension ($N.m^{-1}$)
Ω_{int}	interfacial surface area (m^2)
Ω_{lngem}	logarithmic mean value of surface area

LIST OF CHEMICALS

Ac^-	acetate
Alamine 336	mixture of tertiary amines with alkyl chains varying from C8 to C10
Aliquat 336	mixture of quaternary ammonium compounds with alkyl chains (R) varying from C8 to C10
CTA	cellulose triacetate
CYANEX 272	di(2,4,4-trimethylpentyl)phosphinic acid
CYANEX 302	di(2,4,4-trimethylpentyl)monothiophosphinic acid
CYANEX 301	di(2,4,4-trimethylpentyl)dithiophosphinic acid
D2EHPA	di(2-ethylhexyl)phosphoric acid
DBP	dibutylphosphoric acid
DOX	decanaloxime
DTPA	di(2-ethylhexyl)dithiophosphoric acid
EDTA	ethylenediaminetetraacetic acid
EHO	2-ethylhexanal oxime
ETFE	ethylenetetrafluoroethylene
LIX 63	5,8-diethyl-7-hydroxy-6-dodecanone oxime
LIX 84-I	2-hydroxy-5-nonylacetophenone oxime
LIX 860-I	5-dodecylsalicylaldoxime
MCH	methylcyclohexane
NaCl	sodium chloride
Na_2CO_3	sodium carbonate
(Na, H)Ac	acetate buffer
$(NH_4)_2SO_4$	ammonium sulphate
NaOH	sodium hydroxide
NPOE	2-nitrophenyl octyl ether
PC-88A	mono(2-ethylhexyl)ester of 2-ethylhexylphosphonic acid
PP	polypropylene
PVC	polyvinylchloride
PVDF	polyvinylideendifluoride
PTFE	polytetrafluoroethylene
TBP	tri-n-butylphosphate

TBEP	tri(2-n-butoxyethyl)phosphate
TBPO	tri-n-butylphosphine oxide
THF	tetrahydrofurane
TNOA	tri-n-octylamine
TOPO	tri-n-octylphosphine oxide
Versatic 10	synthetic, highly branched-C10 tertiary carboxylic acid

Chapter 1

INTRODUCTION

Heavy metal ions are often present in different types of effluent streams resulting from the metal finishing industry, textile industry, mining industry and many other branches [1_1-1_3]. These effluent streams are important sources of pollution because of their high toxicities and wide environmental spreading.

The rapidly increasing environmental consciousness has led to considerably tightened environmental standards in many countries. Urged by stringent requirements, the steel industry has made substantial investments in environmental technology. In Germany, for instance, from 1975 until 1984 ca. 1.2×10^9 Euro (10% of the steel industry's resources for new investments) were spent on environmental protection with a division of capital expenditure of 67.7% for air pollution control, 21.4% for water pollution control, 9.5% for noise reduction and 1.4% for waste management [1_1]. The "MIRA" or Flemish Environmental Report describes, analyses and evaluates the state of the Flemish environment. In addition, the "MIRA" also discusses the environmental policy and future developments. Figure 1-1 gives an overview of the emissions of heavy metals in surface water, which has been reported in "MIRA-T 2006" [1_4]. The emissions of the metal ions in 1998 are taken as a reference (1998=100).

Figure 1-1 shows a general decrease of metal pollution of surface water between 1998 and 2005. Only cadmium, mercury and lead deviate from the above conclusions, although a decrease (small decrease for lead) was noticed in 2005 compared to 1998. The efforts of several companies, which were mainly driven by a policy of taxes, contribute to the general decrease of metal pollution of surface water. The aim of the Flemish Environmental Policy plan, namely MINA-plan 3 (50% reduction in 2010 compared to 1998) has not yet been reached for any metal ion, as also shown in Table 1-1. In addition, it may be noticed that between 2003 and 2005, the decreases are rather limited. To reach the objective of the MINA-plan 3, further efforts are necessary.

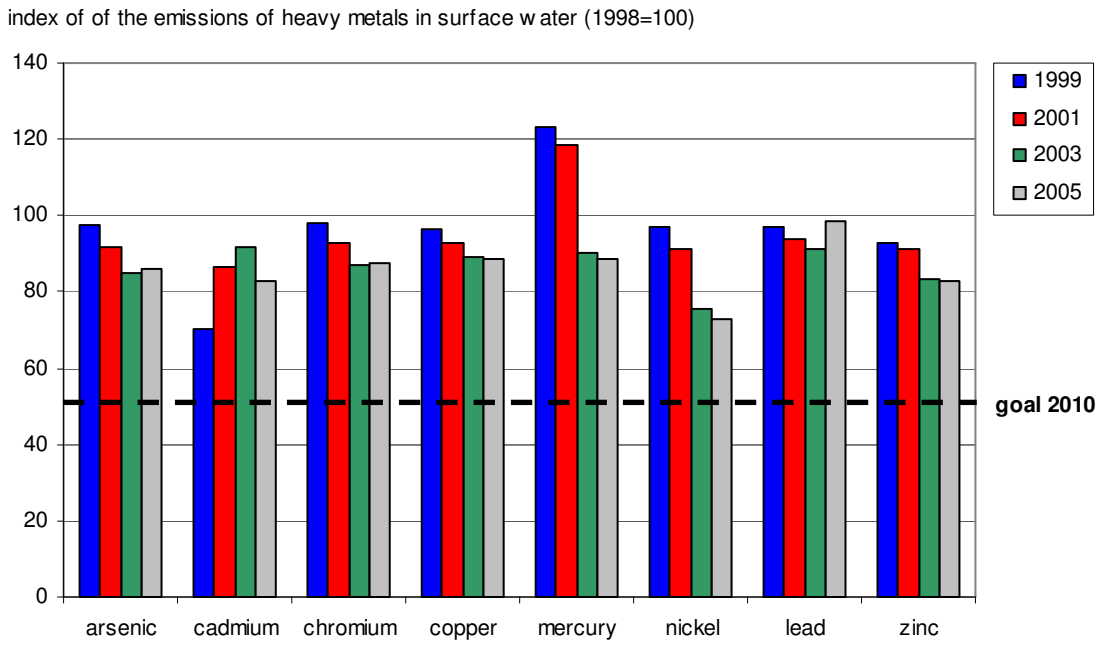

Figure 1-1. Evolution of the emissions of heavy metal ions in surface water from 1998 until 2005 (MIRA-T 2006) [1_4]

Table 1-1. Percentage reduction of the emissions of metal ions in surface water in 2005 compared to 1998 (MIRA-T 2006) [1_4]

%	arsenic	cadmium	chromium	copper	mercury	nickel	lead	zinc
	14	17	13	11	12	27	2	17

The treatment of effluent streams constitutes a crucial part of most industrial processes. Many companies foresee problems when they keep on cleaning their waste water with the conventional environmental technologies. Conventional pollution control or "end-of-pipe" treatment is expensive and environmentally inefficient as it is primarily concentrated on the treatment of residues [1_1]. For environmental regulation, the focus has shifted away from emission reduction through "end-of-pipe" treatment towards integrated approaches. Integrated approaches, viz. membrane processes, consider both treatment and source control to deliver the most cost-effective solutions [1_5]. The Paris Commission has adopted PARCOM-Recommendations on Best Available Techniques and Best Environmental Practice [1_6]. The limits for metal emission in waste water according to the

PARCOM-Recommendation 92/4 are shown in Table 1-2. The limit values should be achieved without any kind of dilution before discharge.

Table 1-2. Maximum discharge values for metal ions following PARCOM-Recommendation 92/4 [1_6]

Metal	Limit ($mg.L^{-1}$)
Chromium (total)	0.5
Chromium(VI)	0.1
Copper	0.5
Lead	0.5
Nickel	0.5
Silver	0.1
Tin	2.0
Zinc	0.6
Cadmium	0.2
Mercury	0.05

Due to the very strict discharge values for metal ions, new technologies are constantly emerging for treating and purifying all kinds of waste water.

Three important approaches must be taken into account:

1) The removal of metals from the effluent streams
2) The achievement of concentrated metal solutions to the level where further processing is economical
3) Conversion of the metal ions into a chemical substance which simplifies eventual recovery

Recycling of metal ions has two major effects upon our society. The recovery of metal ions results in a decrease of the general pollution of the environment. But, recycling also leads to the conservation of natural resources, which is nowadays also an important issue. In addition, innovative technologies can also be implemented in the treatment of product streams, leading to cost-effective operations.

An innovative waste water treatment technique is the Supported Liquid Membrane (SLM) technology. In the next paragraph, the benefits of SLM will be discussed and will be related to the restrictions often encountered with existing technologies.

1.1. SUPPORTED LIQUID MEMBRANES AS AN INNOVATIVE WASTE WATER TREATMENT TECHNOLOGY

The most common form of effluent treatment containing heavy metal ions involves the precipitation of the metals as a hydroxide, a basic salt or as a sulphide. Precipitation is often followed by an additional treatment such as sedimentation and filtration processes. Besides the fact that precipitation is an end-of-pipe treatment, some metals do not precipitate at the neutral pH of disposal because of the formation of aqueous soluble anionic complexes (e.g. molybdate, chromate, …) or the formation of complexes with aqueous soluble organic complexation agents. Also, the selective precipitation of a metal ion from industrial process streams is not always possible. In these cases, other waste water treatment systems are necessary.

Ion exchange resins are also frequently used for purifying waste water. During ion exchange processes, an ion from a solution is exchanged for a similarly charged ion attached to an immobile solid particle. The synthetic organic resins are the predominant type used nowadays because their characteristics can be tailored to specific applications [1_7]. Organic ion exchange resins are composed of high molecular weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium [1_7]. Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionisable group attached to the basic polymer network. It is this functional group that determines the chemical behaviour of the resin [1_7]. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin [1_7]. Once the resin is fully loaded, the metal ions can be desorbed from the resin with concentrated acid (cation exchange resin) or with a concentrated sodium hydroxide solution (anion exchange resin). Although ion exchange resins are frequently used in the industry nowadays, ion exchange processes frequently lack selectivity and there is a limited choice in the kind of functional groups available on commercial resins. Moreover these processes can produce a lot of rinsing water due to the interstitial water within and between the resins beads. Complicated regeneration schemes or techniques are then necessary to avoid unacceptable dilutions.

Other conventional waste water treatment systems include electrically driven processes, viz. electrolysis and electrodialysis. Processes in which an electrical potential

difference acts as a driving force use the ability of charged ions or molecules to conduct an electrical current. Uncharged molecules are not affected by this driving force and hence electrically charged components can be separated from their uncharged counterparts [1_5]. Sometimes, ion exchange membranes are used to control the migration of the ions. Two important types of membranes can be distinguished: cation-exchange membranes allow the passage of positively charged ions and anion-exchange membranes allow the passage of negatively charged ions. The combination of an electrical potential difference and the cation- and anion-exchange membranes can be used in various arrangements. The main process is electrodialysis [1_7]. A number of cation- and anion-exchange membranes are placed in an alternating pattern between a cathode and an anode. When a direct current is applied, the ionic concentration increases in alternating compartments (concentrate) accompanied by a simultaneous decrease in ionic concentration in the other compartments (diluate). The concentrate allows the recuperation of metal ions. An important drawback of electrodialysis is however that low electrical efficiencies are obtained when dilute metal streams have to be treated, resulting in high operating costs.

Solvent extractions offer an alternative for the recuperation of metal ions. However, conventional solvent extraction methods are not frequently used because of high operating costs when compared to the value of the materials recovered. During solvent extraction, the metal ions in an effluent stream are extracted into an immiscible solvent containing a complexation agent or extractant molecule by dispersing one of the immiscible phases as drops in the other phase. This creates a large interfacial area and increases the extraction rate considerably [1_8]. A mixer-settler arrangement provides a single equilibrium stage; the connection of a number of these provide multistage extraction. Regardless of the dispersion-based contacting devices, conventional equipment has many disadvantages: the need for dispersion and coalescence, problems of emulsification, loading limits, high operating costs, etc [1_8]. Furthermore, conventional solvent extraction processes require a high quantity of complexation agents. In the case of special applications which require macrocylic extraction reagents, viz. extraction of precious metals, the chemical costs become too high. Membrane-based solvent extractions appear to eliminate a lot of problems [1_8].

The “Supported Liquid Membrane” technology (SLM) is a membrane-based solvent extraction method that uses a micro-porous hydrophobic membrane as supporting layer. This membrane, often polypropylene, is impregnated with an organic solvent containing the specific carrier molecules for metal ion extraction. At one side of the membrane the effluent stream (feed) is pumped. At the other side, a concentrated acid solution (strip) is circulated.

At the feed/membrane interface, the complexation reaction takes place. The metal complex diffuses through the liquid membrane followed by a decomplexation of the metal complex at the membrane/strip interface. In this way, metal ions are transported from the effluent stream towards a strip solution. In fact, the metal ions are transported against their own concentration gradient due to the concentrated acid (driving force of protons) which allows the metal ions to be effectively concentrated in the strip phase. In this way, dilute metal streams can be treated efficiently. Furthermore, the SLM-technology results, according to the industrial needs, into a strongly reduced disposal of metal waste. This technique not only reduces and avoids waste, but also aims at the recovery of valuable products [1_9]. The vast majority of industrial effluents and waste water, such as mining water, etching or pickling baths, dilute leach solutions generated during hydrometallurgy, electroplating rinse liquors, etc. may carry Ni(II), Cu(II), Zn(II), Co(II) etc. in low concentrations [1_2, 1_9]. The SLM technology offers the possibility to reach the discharge reference values for these metal ions, which is not always the case with other available techniques [1_9]. Furthermore, SLM offers a potential attractive alternative to the conventional processes because it combines the process of extraction and stripping in a single unit operation. Other advantages are the use of a low amount of organic extractant compared to conventional solvent extraction systems and the free choice of organic extractant in contrast to the commercial ion exchange resins which offer only a limited choice of functional groups.

The SLM technology has proven already to be successful for the recuperation of copper(II) ions from industrial effluents [1_2]. For other metal ions, viz. nickel(II) and cobalt(II), the kinetics of the extraction process are still rather limited [1_3, 1_10-1_14]. The essential need for metal ion recovery as well as for the extraction of numerous organic compounds over the last two decades in hydrometallurgy, biotechnology and in the treatment of industrial waste water has lead to significant scientific effort [1_10-1_20] to understand the complexation mechanisms in extraction processes. The results have contributed to establish the mechanisms of many extraction systems, to evaluate the conditions for selective extraction, and in some cases even to predict the type of complex that is formed in a system. At the same time, the extraction circumstances can vary a lot and complexation mechanisms are not always unequivocal [1_10-1_20]. Therefore, the extraction behaviour of transition metals applicable in Supported Liquid Membranes is studied in depth in the present work. Extraction studies are mainly concentrated on the metal ions nickel(II), cobalt(II), copper(II),

iron(II,III) and magnesium(II). A comprehensive discussion of the Supported Liquid Membrane technology will follow in Chapter 2.

1.2. PROPERTIES AND CLASSIFICATION OF THE METAL IONS COPPER(II), NICKEL(II), COBALT(II), IRON(II, III) AND MAGNESIUM(II) ACCORDING TO THEIR ABILITY FOR COMPLEXATION

1.2.1. Main applications of the metals copper, nickel, cobalt, iron and magnesium [1_1]

Iron

Iron is the most widely used metal, yet its price is the lowest of all metals [1_1]. Its annual production exceeds by far that of all other metals combined. It comprises approximately 93% of the tonnage of all the metals used. However, it lacks important properties such as corrosion resistance [1_1]. From the beginning of the nineteenth century, copper, nickel, lead, zinc, and tin and their alloys found use as substitutes for iron in industrial applications that required particular properties in which cast irons and steels were lacking. That is one reason why these metals are known as primary metals [1_1]. The group of secondary metals includes cadmium, cobalt and mercury and the metalloids arsenic, antimony and bismuth. They are mainly recovered as by-products of the mining and processing of the ores of primary metals. They are used worldwide in amounts of about 20 000 tons annually [1_1].

In the recent past, the rapidly increasing environmental consciousness has lead to considerably tightened environmental standards in many countries. Industrial waste often contains iron together with other important primary or secondary metal ions as impurities. In many extraction processes, the recovery of those more expensive metal ions is hindered by the presence of iron. The preceding removal of iron is therefore indispensable.

Copper

Copper is a useful material with a wide range of applications. Because of its excellent electrical conductivity, it is the dominant conductor material [1_1]. Copper is also frequently used in the chemical and food industries because of its high resistance against corrosion, but there is also substantial use of copper in mechanical engineering and increasing interest in

copper as material in building constructions [1_1]. For large quantities of copper solutions at high concentration, recovery of copper can in many cases be economical.

Nickel

As compared to other non-ferrous heavy metals, nickel is stronger, harder, more refractory and more resistant against corrosion [1_1]. The major first uses of nickel are mainly found in the stainless steel production, ferrous alloys, nickel-based alloys and electroplating applications [1_1]. Nickel is used for plating metals with a view to protect them against corrosion and for ornamental purposes. Nickel is also required for the manufacture of certain types of batteries, which are lighter, more compact and dependable in operation than lead batteries. Furthermore, nickel catalysts find their applications in many chemical processes.

Cobalt

Pure metallic cobalt has few applications, but its use as an alloying element and in chemicals makes it a strategically important metal [1_1]. Cobalt chemicals, among their many applications, are used as pigments in glass, ceramics, and paint industries; as catalysts in the petroleum industry; as paint driers; and as trace metal additives for agricultural and medical use [1_1]. About 36% of the worldwide annual production of cobalt is converted into chemicals [1_1]. The numerous applications and strict legislations on metal waste disposal emphasize the need for optimized waste water treatment systems.

Magnesium

Magnesium differs from the previous discussed metals because it is not a transition metal ion, but it belongs to the Group IIA(2) Elements. Anyhow, it is interesting to note the extraction behaviour of the alkaline earth metal magnesium(II) towards the selected extractants.

1.2.2. Classification of metal ions according to their ability for complexation [1_21-1_23]

During a complex forming reaction, the solvent molecules surrounding the metal ion M^{n+} may be successively exchanged for other ligands or molecules HL, which leads to the complex ML_n (in its simplest form) where n indicates the number of ligands in the complex. Metal ions form complexes with different composition, structure and stability with various complexing ligands. The coordination number depends on the oxidation state of the metal ion, but very often also on the nature of the ligand [1_21].

An overview of the most common geometries of nickel(II), cobalt(II), copper(II) and iron(III, II) complexes is given in Table 1-3 [1_22].

Table 1-3. Most common coordination numbers and geometries of the metal complexes [1_22]

Metal ion	Coordination number	Geometry
Ni(II)	4	square
	4	tetrahedral
	6	octahedral
Cu(II)	4*	Tetrahedral (distorted)
	4*	square
	6*	distorted octahedral
Co(II)	4	tetrahedral
	6	octahedral
Fe(II)	6	octahedral
Fe(III)	6	octahedral

* These three cases are often not sharply distinguished

Metal ions can be divided into three groups according to their complex-forming ability [1_21-1_23]. The first group consists of metal ions with a noble-gas electronic configuration. This group includes alkali metal, alkaline earth metal and lanthanide and actinide ions. Complexation is mainly accomplished through the formation of electrostatic bonds. These metal ions preferentially form complexes with ligands containing oxygen donor atoms. The stability of the complex increases with a higher charge density in the metal ion because the bonds are mainly ionic [1_21].

The second group includes copper(I), silver(I), gold(I), mercury(II), platinum(II) and palladium(II), the ions of which are capable to form covalent bonds. In contrast to the ions of the first group, highly stable complexes can be formed with these ions. In the first group, the charge and ionic radius is important in the complex formation. In the second group the electronegativity plays a major role. Metals of this second group form stable complexes with ligands containing sulfur, arsenic and phosphorus [1_21].

The third large group contains transition metal ions with partially filled orbitals. The properties of these ions are situated between those of the two preceding groups. The charge and radius of the ion as well as the stabilization due to orbital splitting are of importance. The transition metal ions with partially filled orbitals mainly bind nitrogen- and oxygen-containing ligands [1_21].

The investigated metal ions belong to the main transition group or d-block, which includes the elements that have partly filled 3d shells only either in the ground state of the free atom or in one or more of their chemically important ions. This group of elements is also called the first transition series. Only magnesium(II) differs from the other investigated metal ions because it belongs to the Elements (II, A2) [1_22].

The metal ions in the first group are also considered as “hard” acids whereas those in the second group are “soft” acids [1_21, 1_23]. A high electronegativity and low polarizability are characteristic features of the hard acids whereas the opposite is true for the soft acids. Complexes of high stability are formed between hard acids and hard bases and soft acids and soft bases. The properties of the third group are intermediate between those of the first and second group. A classification of some metal ions and ligands as hard and soft acids and bases is shown in Table 1-4 [1_23].

The properties of the donor atom of the ligand is of importance in determining the complex stability. These are, in order of increasing electronegativity: As, P < C, Se, S, I < Br < N, Cl < O < F. In general, metal ions of the first group form stable complexes with hard bases and those of the second group with soft bases as shown in Table 1-4 [1_23].

There exists also a correlation between the complexing ability and Brönsted basic strength of ligands of similar structure which contain the same donor atom [1_21]. The smaller the dissociation constant of the conjugated acid, the stronger is the ligand as a base. This usually results in a greater stability of the complex formed.

Stable complexes can be formed if a chelating ligand is used [1_21]. The most stable chelates involve the formation of 5- or 6-membered rings. However, steric factors may affect the complex formation. The chelate formation can be inhibited if the ring formation is completely or partially hindered. The stability of chelates formed with multidentate ligands is usually higher than that of complexes formed with similar unidentate ligands [1_21].

Table 1-4. Classification of some metal ions and ligands as hard and soft acids and bases (after Pearson) [1_23].

Electrophiles	Nucleophiles
Hard acids	*Hard bases*
H^+, Li^+, Na^+, K^+	H_2O, OH^-, F^-, PO_4^{3-}, SO_4^{2-}
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	CO_3^{2-}, ClO_4^{2-}, NO_3^-, Cl^-
Al^{3+}, Sc^{3+}, Ga^{3+}	ROH, RO^-, R_2O, NH_3, RNH_2
Cr^{3+}, Co^{3+}, Fe^{3+}, Ce^{3+}	CH_3^-, N_2H_4
Si^{4+}, Ti^{4+}, Cr^{4+}, Th^{4+}	
Soft acids	*Soft bases*
Cu^+, Ag^+, Au^+, Tl^+, Hg^+	R_2S, RS^-, $S_2O_3^{2-}$, CN^-
Cd^{2+}, Hg^{2+}, Pd^{2+}, Pt^{2+}	I^-, SCN^-, R_3P, R_3As
Ti^{3+}	H^-, R^-
Pt^{4+}	
Borderline	*Borderline*
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	Cl^-, Br^-, N_3^-, NO_2^-, SO_3^{2-}
Pb^{2+}, Sn^{2+}, Ru^{2+}, Os^{2+}	$PhNH_2$
Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}	

1.3. INFLUENCE OF MIXED EXTRACTANT SYSTEMS AND AQUEOUS PHASE ADDITIVES ON THE EXTRACTION BEHAVIOUR OF COBALT(II), COPPER(II), NICKEL(II), IRON(II, III) AND MAGNESIUM(II) IN DIFFERENT TYPES OF SOLVENTS

Acidic extractants are frequently used for the extraction of metals ions such as cobalt(II), copper(II), nickel(II), iron(II, III) and magnesium(II). These acidic extractants or carrier molecules belong to the organophosphorous type reagents, e.g. D2EHPA [di(2-ethylhexyl)phosphoric acid], CYANEX 272 [bis(2,4,4-trimethylpentyl)phosphinic acid], CYANEX 302 [bis(2,4,4-trimethylpentyl)monothiophosphinic acid] and CYANEX 301 [bis(2,4,4-trimethylpentyl)dithiophosphinic acid], or to the hydroxyoxime-based ligands, viz. LIX 860-I [5-dodecylsalicylaldoxime] [1_2-1_3, 1_9, 1_12, 1_16-1_20]. LIX 860-I is for instance a very efficient extraction reagent for copper(II) [1_2]. For other metal ions, viz. nickel and cobalt, the kinetics of the extraction process are rather limited [1_3, 1_10-1_14].

In Chapter 3, liquid-liquid extraction results will be discussed of nickel(II), copper(II), cobalt(II), magnesium(II) and iron (II, III) with D2EHPA, CYANEX 301 and LIX 860-I as extraction reagents. Furthermore, FT-IR and UV-VIS spectrofotometric analyses will be performed to gain insight in the complexation behaviour of the different metal ions towards the various extractants.

At first, two different organic solvents will be investigated, viz. the non-polar solvent hexane and a higher alcohol, 1-decanol. The diluent is not only a solvent for the extractant and extracted metal complex, but can also be a participant in the extraction process [1_24]. The diluent may interact with the extractant molecules, which changes the extraction performance of the extractant. On the other hand, interaction with the extracted metal complex may change the composition of the complex through coordination and/or substitution of the diluent molecules [1_24]. The nickel ion, with a coordination number of 6, tends to retain several water molecules in its first coordination sphere. Higher alcohols are likely to replace the water molecules and can enhance nickel extraction [1_24]. In Chapter 3, hexane as well as 1-decanol will be investigated to study the effect of the diluent on the extraction efficiency of the different metal ions and to study if changes in coordination behaviour occur.

Combining two or more extractants can improve the extraction efficiency of some metal ions considerably [1_10-1_13, 1_25]. Therefore, the synergistic effect of mixtures of extractants, such as organophosphoric acids and chelating oximes, will be investigated for

copper(II), nickel(II), cobalt(II), iron(III, II) and magnesium(II) in Chapter 3. Synergism occurs if a mixture of extractants produces an extraction percentage which is bigger than the sum of the extraction percentages obtained with each extractant independently [1_25]. Among the different extractant combinations in synergistic mixtures, mixtures of acidic carriers and oximes have been used extensively, whereas combinations of two acidic extractants are less common [1_10-1_13, 1_25]. One of the first examples consisted of mixtures of the aliphatic hydroxyoxime LIX 63 [5,8-diethyl-7-hydroxy-6-dodecanone oxime] and D2EHPA for the separation of copper and cobalt from nickel in sulphate media [1_10]. In general, synergism has been shown to occur in many mixed solvent systems, but the actual mechanisms involved are still largely unresolved [1_10-1_13, 1_25]. On the one hand, the extractants can cooperate to increase the extraction efficiency. Interactions of the second carrier with the extracted metal complex can occur for instance by replacement of the coordinated neutral extractant molecules and/or water molecules or by transformation of the coordination geometry. These changes in coordination properties may enhance the complex solubility in the organic phase and change the extraction and/or stripping behaviour for certain species and its selectivity [1_10]. On the other hand, the addition of a second carrier may exhibit a deleterious influence upon the extraction equilibrium when the second carrier can interact with the extractant through the formation of hydrogen bonds [1_10]. Such interactions therefore compete with the metal extraction reaction. The possible effects of mixtures of extractants on the extraction behaviour and coordination behaviour of the metal ions copper(II), nickel(II), cobalt(II), iron(III, II) and magnesium(II) in hexane and 1-decanol will be investigated in Chapter 3.

Another method for improving the extraction performance implies the introduction of certain anionic ligands to the aqueous solution containing metal ions, viz. acetate ions [1_26]. In fact, in the case of waste water treatment by means of liquid membranes, certain useful ligands may already be present in the waste water, thereby reducing the reagent cost. The selected additive should be a weak complexing agent for the metal ions. A strong complexing agent will prevent the extraction process. A study on the extraction of cobalt(II) [1_26] showed that adding acetate to the aqueous solution greatly accelerated the extraction. In fact, the water molecules in the hexaaqueous cobalt(II) complex can be replaced by the anionic ligand [1_26]. Furthermore, the anionic ligand has a hydrophobic-hydrophilic nature. Therefore, it exhibits a surface-active property. The anionic ligand-metal complex tends to populate at the aqueous-organic interface more than the hydrated metal ions do. In this way, the metal ions are relatively concentrated at the feed/membrane interface. This is favourable

for the membrane process and is called ligand-accelerated liquid membrane extraction. Besides the hydrophobic-hydrophilic nature of the anionic ligands, a buffer can be formed, which is interesting for the extraction of metal ions such as nickel(II) and cobalt(II). Those metal ions are extracted at higher pH values compared to copper(II) and iron(III) [1_9]. In Chapter 3, the effect of the addition of acetate to the aqueous phase will be investigated for the different metal ions under investigation. In addition, infrared and UV-VIS spectrophotometric studies will be performed to verify if acetate/acetic acid also migrates into the organic phase.

1.4. DETERMINATION OF THE STOICHIOMETRY OF COPPER(II), NICKEL(II), COBALT(II) AND IRON(III) COMPLEXES WITH ORGANOPHOSPHOROUS ACIDS AND HYDROXYOXIME-BASED LIGANDS

In Chapter 4, two methods will be studied to determine the stoichiometry of the metal-organic complexes. Some authors [1_3, 1_15-1_20] have tried already to determine the stoichiometry of some metal complexes by slope analysis techniques, but no overview has been given concerning the ligand-to-metal ratios of the metal complexes under the same experimental circumstances. Also, the extraction chemistry is not always unequivocal [1_3, 1_15-1_20].

The first method that will be studied in Chapter 4, Job's method or the method of continuous variation, is a useful spectrophotometric method for elucidating the composition of complex ions in solution [1_21, 1_27]. Analytical methods based on the measurement of light absorption can be used to study complexation equilibria, since they are suitable for the selective determination of very small concentrations of certain species. Job's method or the method of continuous variation makes use of the fact that the optical properties of solutions containing complexes usually differ from those of the constituent ions or molecules. The change in optical behaviour is closely related to the formation of coordinate bonds [1_21, 1_27]. The principle of the method is that the mole ratio of the metal ion and ligand is varied between 0 and 1 at a total constant concentration of metal ion and ligand. The absorbance of the solutions of different composition is then measured and plotted against the mole-fraction of metal ion or ligand. If only one complex has been formed, the composition of the metal complex can be deduced from the plot of the absorbance versus mole-fraction of metal ion or ligand. Job's method will be used in the present work to determine the stoichiometry of nickel(II), cobalt(II), copper(II) and iron(III) complexes with D2EHPA, CYANEX 272,

CYANEX 302, CYANEX 301 and LIX 860-I. In addition, the distribution coefficients and extraction constants of the metal-organic complexes will be determined.

During the progress of the experimental work, the results of Job's method showed that sometimes additional compounds are participating in the complexation process. Especially in the case of iron(III), it has been observed that hydrolysis can influence the extractant:metal ratio of the metal complex. In order to prevent possible hydrolysis, the conventional liquid-liquid extraction process is therefore compared with the complexation behaviour under water-free circumstances (see Chapter 4). During this experimental procedure, no liquid-liquid extractions were performed, but the anhydrous metal salt was added directly to the organic phase. By following up the release of hydrogen chloride during complexation, formed by the acidic proton of the extractant and the chloride anion of the metal salt, a correlation can be obtained with the number of extractant molecules present in the coordination geometry of the metal ion. FT-IR as well as UV-VIS spectrophotometric analysis will be used to gain further insight in the complexation characteristics.

1.5. SUPPORTED LIQUID MEMBRANES (SLM) VERSUS POLYMER INCLUSION MEMBRANES (PIM) AND IMMOBILIZED LIQUD MEMBRANES (ILM)

Whereas in Chapter 3 and 4, the more fundamental aspects of metal extraction will be studied, Chapter 5 will deal with a more technological study to recuperate nickel(II) with Supported Liquid Membranes (SLM). The limit for nickel(II) emission in waste water according to the PARCOM-Recommendation 92/4 is 0.5 $mg.L^{-1}$ [1_6].

The most promising liquid ion exchangers for the extraction of nickel(II) are organophosphorous acid derivatives [1_3, 1_10, 1_28], hydroxyoximes [1_11-1_13] and macrocyclic compounds [1_29]. However, much attention has been drawn to the use of combinations of different extractants to improve the fluxes of nickel(II), as mentioned already in paragraph 1.3. In Chapter 5, conventional liquid-liquid extraction methods will be used to determine the extraction efficiency of nickel(II) with mixtures of an organophosphorous acid and an aromatic hydroxyoxime-based ligand. In addition, the selectivity of the extraction of nickel(II) compared to alkaline earth metals, e.g. magnesium(II) will be evaluated. As solvent, the typical industrial solvent, kerosene, will be used. Aliphatic hydrocarbons of higher boiling point are suitable membrane solvents [1_30]. These mixtures of extractants will also be implemented in an SLM lab-scale environment. Flat membranes as well as hollow fiber modules will be used throughout the research.

Furthermore, a mixed extractant system will be tested for the recovery of nickel(II) from real effluents streams created by the metal finishing industry. The aim of the application on real effluent streams is to show that Supported Liquid Membranes are able to reach the PARCOM-levels [1_6]. The three types of nickel bath rinse solutions which are encountered in industrial plating shops are resulting from a Watt's nickel bath, a nickel sulphamate bath and an electroless nickel bath. These nickel baths are widely used for rapid plating of ductile nickel with high cathode and anode efficiencies. Finally, the stability of the mixed extractant system will be evaluated.

In Chapter 6, an introduction will be given of Polymer Inclusion Membranes (PIM) and Immobilized Liquid Membranes (ILM) as innovative technologies for the recuperation of metal ions. The goal of these novel membrane types is to maximize the membrane fluxes of the corresponding Supported Liquid Membrane system, whereas the extraction efficiency and selectivity is maintained.

Polymer Inclusion Membranes are formed by casting a solution containing an extractant, a plasticizer and a base polymer such as cellulose triacetate (CTA) or polyvinylchloride (PVC) to form a thin, flexible and stable film [1_31-1_33]. The resulting self-supporting membrane can be used to separate selectively metal ions in a similar way to that of SLM. Both SLM and PIM involve the selective transport of a target species from one aqueous solution to another by means of the membrane. However, because PIM membranes are distinctively different from SLM in their composition and morphology, the actual bulk diffusion mechanisms within the membrane can be quite different. In fact, because the carrier is not covalently bound to the base polymer, it may be assumed that the actual diffusion mechanism in PIM membranes is intermediate between mobile carrier diffusion and fixed-site jumping [1_31-1_32]. It is also worth mentioning that PIM membranes have been used for more than 30 years in the form of polymer membrane ion-selective electrodes (ISEs) [1_31]. In SLM, the capillary force or interfacial tension is responsible for the bonding of the membrane liquid phase to the supporting pores. For PIM membranes, it is most likely that carrier, plasticizer and base membrane skeleton are bound to one another by a form of secondary bonding such as hydrophobic, van der Waals or hydrogen bonds. These secondary bonds are much stronger than interfacial tension or capillary forces and are only favorably in view of a long-term stability [1_31]. A lot of research has been focused on the extractant, Aliquat 336, which consists of a mixture of quaternary ammonium compounds with alkyl chains (R) varying from C8 to C10 [1_31-1_33]. The advantage of Aliquat 336 is that it

can also play the role of plasticizer. In this way, no additional plasticizer must be added. However, the main goal of the work of Chapter 6 is to develop a novel system which utilizes LIX 860-I as extractant in a PIM membrane for the recuperation of copper(II) and evaluate its potential abilities compared to the Supported Liquid Membrane technology.

The second part of Chapter 6 gives an introduction of Immobilized Liquid Membranes, also called fixed-site carrier membranes. In ILM, the extractant molecules are covalently attached onto the polymer backbone. The fixed-site jumping mechanism has been proposed to describe the facilitated transport process in a solid membrane where mobility of the carrier is restricted due to the covalent attachment of the carriers onto the polymer [1_31]. Therefore, the extractant concentration must be sufficiently high so that a continuous chain across the membrane can be formed. Only then, an efficient transport of the solutes of interest can be assured [1_31]. In order to anchor the carriers onto the polymer matrix, the polymer must possess functional groups for modification. In SLM, polypropylene is frequently used as micro-porous hydrophobic membrane. However, polypropylene membranes do not possess functional groups ready for modification. These functional groups can only be implemented by plasma treatment or special radiation techniques, which is beyond the scope of this work [1_34]. Therefore, a screening is made of available membranes which can be modified by a chemical reaction. Two membrane types will be evaluated for modification, namely an ethylenetetrafluoroethylene membrane (ETFE, Solvay) functionalized with vinylbenzylchloride and a polysulfone membrane (Desal E-500, Desalination Systems). The first step in the modification process is to implement primary amine functional groups in both membranes, followed by the anchoring of a chelating agent, such as LIX 860-I or 8-hydroxyquinoline [1_35-1_39]. In the case of the functionalized ETFE membrane, primary amine groups can be achieved through reaction with liquid ammonia [1_35-1_36]. General methods of introducing functional groups into polysulfones involve a direct lithiation or a dual process of bromination/lithiation, as well as the amination of polysulfone by novel azide intermediates [1_37-1_39]. These modifications make use of lithiated polymer intermediates which are reactive to a variety of electrophiles. In literature [1_37-1_39], modifications are usually performed in homogeneous reaction mixtures (dissolution of the powder form of the polymer in the reaction mixture) followed by the subsequent formation of a polymer film. In the present work, the goal is to evaluate the direct modification of a polymer film.

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Chapter 2

SUPPORTED LIQUID MEMBRANES

Liquid membranes have drawn a lot of attention during the past decades for the separation and concentration of metal ions due to its ease of operation and selectivity advantages. Applications can be found in the industrial and analytical fields as well as in waste water treatment [2_1]. The separation of metals by liquid membranes has been actively investigated for its application in hydrometallurgy [2_2]. In 1986, a process to recover zinc from waste streams at a textile plant in Austria was developed as the first liquid membrane process on a commercial scale [2_2]. The attraction of liquid membranes for extraction processes is due its several advantages. The molecular diffusion in liquids is generally several orders of magnitude faster than in solids. Liquid membranes can also be designed to be highly selective to specific solutes and relatively small quantities of carrier or extractant are needed. Therefore, low amounts of highly selective, relatively expensive agents can be used. Furthermore, a maximum driving force can be created, which avoids the use of multistage processes in liquid extraction. A major disadvantage of liquid membranes - in comparison to solid membranes - is the lack of the long-term stability [2_3].

A uniform classification of the different types of liquid membranes is difficult due to the variety of membranes and processes. In this work, the classification of liquid membranes depends on the occurrence of the liquid membrane as a pure liquid phase or if a polymeric support is involved in the process [2_4]. This leads to two major classes: Non-Supported Liquid Membranes and Supported Liquid Membranes (SLM). In the case of Non-Supported Liquid Membranes, the most common types are Emulsion Liquid Membranes (ELM) and Bulk Liquid Membranes (BLM) [2_4].

Supported Liquid Membranes are prepared by impregnating a hydrophobic micro-porous support with a suitable organic solvent. The porous membrane only serves as a framework or supporting layer for the liquid film, which is immobilised within the pores of the porous membrane [2_5].

In the case of Emulsion Liquid Membranes (ELM), two immiscible phases, water and oil, are mixed vigorously [2_5]. This leads to the formation of emulsion droplets, which are stabilised by the addition of a surfactant. In this way, a water/oil emulsion is obtained. To this emulsion, an aqueous phase is added in such a way that a water/oil/water emulsion is formed. In this concept, the oil phase serves as liquid membrane [2_5].

The third type are Bulk Liquid Membranes (BLM). In Bulk Liquid Membranes, two miscible aqueous liquids (feed and strip) are separated by a third immiscible organic liquid (carrier) [2_2]. These membranes are frequently used to investigate novel carriers, carrier systems or transport mechanisms. Their main function is to optimise data for SLM and ELM. The principal disadvantage of traditional Bulk Liquid Membranes is the low interfacial surface areas and mass transfer rates as compared to SLM and ELM [2_2].

This study is mainly based on the extraction of metal ions from industrial waste water with the Supported Liquid Membrane Technology, although the fundamental research results can also be applied for the other types of liquid membranes. The basic concept of extraction and stripping is similar to the conventional liquid-liquid extraction process. The most important difference is that extraction and stripping or complexation and decomplexation are performed in a single unit operation during SLM.

An organic carrier solution is held in the pores of a micro-porous membrane by capillary forces. This “liquid membrane” serves as a barrier between the feed and receiving phase (see Figure 2-1) [2_6].

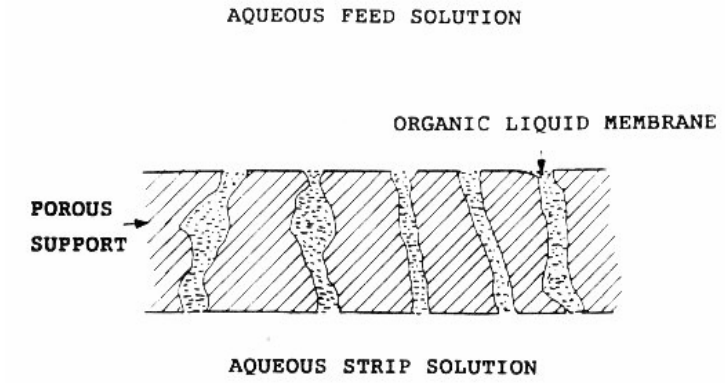


Figure 2-1. Supported organic liquid membrane in a micro-porous film [2_6]

The SLM-feature of simultaneous extraction and stripping removes the equilibrium limitation inherent in solvent extraction. Therefore, the complete removal of a metal ion from the effluent can be achieved with a single-step SLM extraction.

The type of carrier, solvent and supporting layer determines the efficiency of the transport of a solute through a Supported Liquid Membrane. The succeeding paragraphs therefore provide an intensive discussion of the different components of the Supported Liquid Membrane technology. Definitions will be given for the permeation and fluxes of a metal ion through a Supported Liquid Membrane. Furthermore, different configurations and new developments will be discussed and some critical considerations concerning the stability of the technology will be given. But, first of all, detailed descriptions of the different transport mechanisms in liquid membrane processes will be provided.

2.1. TRANSPORT MECHANISMS IN LIQUID MEMBRANE PROCESSES

A membrane process requires two bulk phases, separated by a third phase, the membrane. This membrane can be defined as a semi-permeable barrier. The membrane controls the exchange of mass between the two bulk phases in a membrane process. A particular component in bulk phase I is allowed to be exchanged in preference to the other. Bulk phase II is enriched with that particular species, while bulk phase I is depleted of it. A membrane process therefore allows selective and controlled transfer of species from one bulk phase to another bulk phase with the membrane as separation phase [2_6].

One or more driving forces facilitate the transport of the particular species through the membrane. Species can be transported from a region of high solute concentration to a region of low solute concentration by diffusion, following the first Fickean law:

$$J = -D\frac{\partial c}{\partial x} \tag{2-1}$$

where $\frac{\partial c}{\partial x}$ = concentration gradient ($g.m^{-4}$)

J = flux ($g.m^{-2}.h^{-1}$)

D = diffusion coefficient ($m^2.h^{-1}$)

The flux J is proportional to the concentration gradient across a phase with thickness x (m) [2_6]. This means that the diffusion of a species through a liquid membrane will stop as soon as the concentrations at both sides of the membrane become equal. This is called unfacilitated transport.

Two other transport mechanisms in liquid membrane processes can be distinguished [2_4-2_6]:

1) type I facilitation: in order to maintain the transport of solutes from bulk phase I towards bulk phase II, the diffusing species react with a chemical reagent in the receiving phase resulting in a compound that cannot move back towards phase I.
2) type II facilitation: another type of transport mechanism is needed in the case that the species to be removed are not soluble in the organic membrane phase. This type of transport is also called carrier-mediated or carrier-facilitated transport. The addition of a complexing agent to the membrane phase accelerates the transport of a specific component. Both coupled and un-coupled transport can be distinguished.

These two transport mechanisms will be discussed in detail in the succeeding paragraphs.

2.1.1. Type I facilitation [2_6]

In this type of facilitation, the diffusing component reacts with a chemical reagent in the receiving phase and forms a product that cannot diffuse back through the membrane [2_6]. This type of facilitation can be illustrated by the extraction of phenol from waste water as shown in Figure 2-2 [2_6].

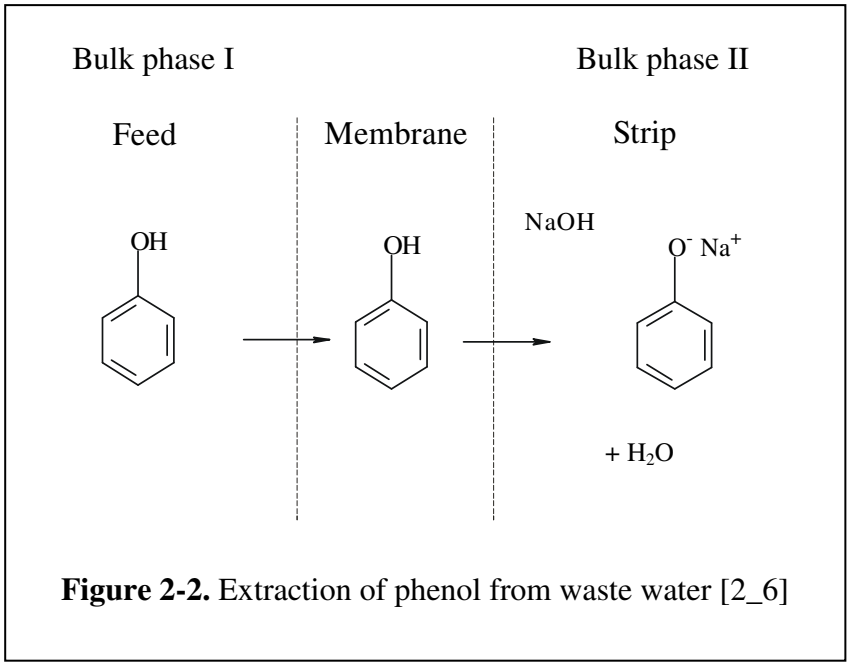


Figure 2-2. Extraction of phenol from waste water [2_6]

Phenol, present in bulk phase I (feed phase), dissolves in a membrane oil phase. Due to a concentration gradient, phenol diffuses across the membrane phase into a NaOH-containing bulk phase II (receiving or strip phase), where it reacts with NaOH to form sodium phenolate.

Since the ionic sodium phenolate is not soluble in the membrane oil phase, it is trapped in the receiving phase. The driving force is the phenol concentration difference between the feed phase and the receiving phase. The reaction maintains the phenol concentration at zero in the receiving phase, resulting in a high driving force and a high extraction rate [2_6].

2.1.2. Type II facilitation

Another type of transport mechanism is needed in the case that the species to be removed are not soluble in the organic membrane phase. This type of facilitation is also called carrier-facilitated transport [2_6]. The species are carried across the membrane phase by incorporating a "carrier" compound (complexing agent or extractant) in the membrane phase. This organic carrier molecule can react selectively and reversibly with the solute. Studies of facilitated transport originated from biochemistry using natural carriers in cell walls [2_4]. Coupled as well as un-coupled transport can be distinguished. The majority of liquid membranes for metal ion separation follow a coupled transport mechanism, which involves the presence of two components [2_6]. Coupled transport can be further subdivided into:

1) co-coupled transport: the two components are moving in the same direction.
2) counter-coupled transport: the two components are moving in opposite directions.

The coupled transport mechanism offers the possibility of transporting a component against its own concentration gradient.

2.1.2.1. Un-coupled transport

If the species to be separated are not soluble in the organic membrane phase, a carrier is added to the liquid membrane. This results in a carrier-solute complex, which readily dissolves in the organic phase. No other components are involved in the process [2_6]. The transport is driven by the concentration gradient of the solute and will stop as soon as the concentration in both feed and receiving phases become equal. This un-coupled transport

mechanism can be illustrated by the carrier-mediated transport of sugars through a liquid membrane containing methyl cholate [2_7], which is shown in reactions (2-2) and (2-3) and in Figure 2-3.

Extraction reaction:

$$S_a + C_o \rightarrow CS_o \tag{2-2}$$

Stripping reaction:

$$CS_o \rightarrow C_o + S_a \tag{2-3}$$

where subscript a and o represent the aqueous and organic phase, respectively. S and C represent respectively the sugar type and the carrier methyl cholate.

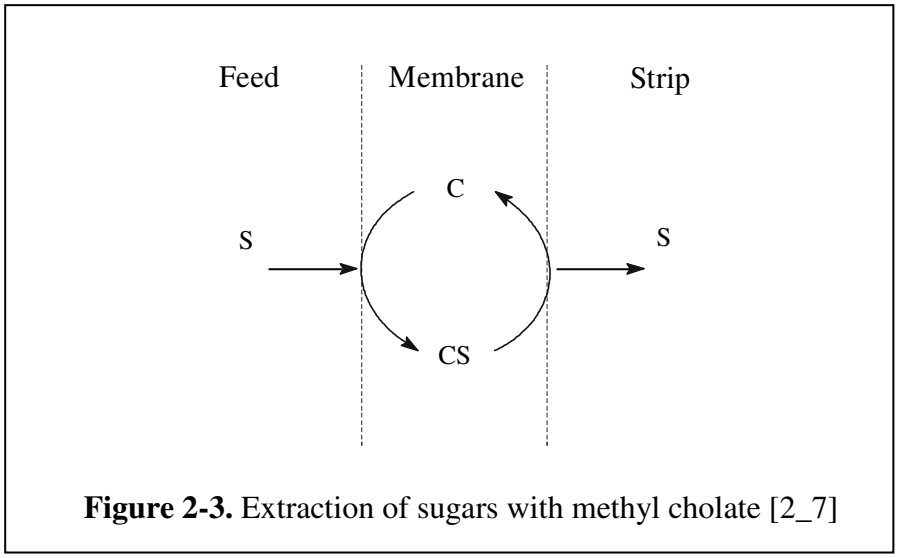


Figure 2-3. Extraction of sugars with methyl cholate [2_7]

At the feed/membrane interface, a complex is formed between the sugar and methyl cholate. The complex diffuses through the liquid membrane into the direction of the strip phase. The complex is dissociated at the membrane/strip interface.

2.1.2.2. Co-coupled transport

The co-transport cases include for instance the extraction of dichromate with a tertiary amine [2_6] and the extraction of alkali metal ions with crown ethers [2_8].

Dichromate extraction with a tertiary amine

The transport of dichromate through liquid membranes containing tertiary amines is based on the co-transport mechanism [2_6]. The transport of dichromate is coupled to the transport of protons in the same direction following the extraction (2-4) and stripping reaction (2-5), respectively, in order to maintain the electrical neutrality in the membrane phase [2_6]. Stripping with a base regenerates the free amine in the membrane, which can react again with additional metal ions in the feed phase as also illustrated in Figure 2-4.

Extraction reaction:

$$2H^{+}_{a} + Cr_2O_7^{2-}{}_{a} + 2R_3N_o \rightarrow (R_3NH)_2Cr_2O_{7o} \qquad (2\text{-}4)$$

Stripping reaction:

$$(R_3NH)_2Cr_2O_{7o} + 4(Na^{+} + OH^{-})_a \rightarrow 2R_3N_o + 2(2Na^{+} + CrO_4^{2-})_a + 3H_2O_a \qquad (2\text{-}5)$$

where R_3N is the tertiary amine.

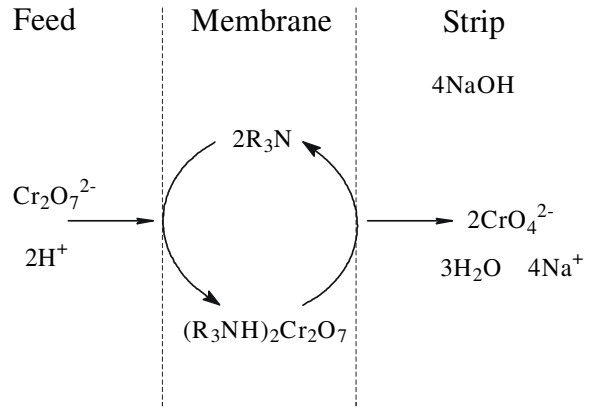


Figure 2-4. Dichromate extraction with tertiary amines [2_6]

Extraction of alkali metal ions with a crown ether

During the extraction of alkali metal ions with crown ethers, the fluxes of alkali metal ions are in the same direction as those of the anionic counter-ions, viz. the extraction of (Na, K) permanganates by 18-crown-6 ether (see Figure 2-5) from water into 1,2-dichloroethane [2_8]. The transport mechanism is shown in Figure 2-6 and in the

extraction (2-6) and stripping reaction (2-7). As strip phase, deionised water was used [2_8]. A high concentration of the counter-ion will maintain the extraction process.

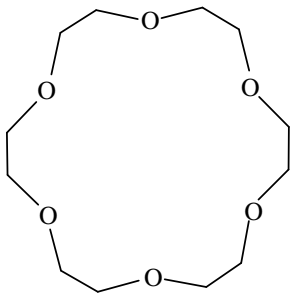


Figure 2-5. Structure of 18-crown-6 ether

Extraction reaction:

$$K^+ + MnO_4^- + L \rightarrow KLMnO_4 \tag{2-6}$$

Stripping reaction:

$$KLMnO_4 \rightarrow K^+ + MnO_4^- + L \tag{2-7}$$

Where L denotes the ligand, 18-crown-6 ether.

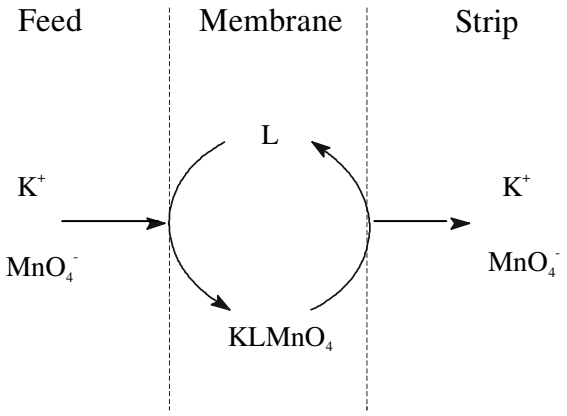


Figure 2-6. Transport of potassium permanganate by 18-crown-6 ether from water into 1,2-dichloroethane [2_8]

2.1.2.3. Counter-coupled transport

This type of facilitation can be illustrated by the removal of copper from industrial effluents with an acidic carrier molecule, viz. 5-dodecylsalicylaldoxime or LIX 860-I (Cognis) (see Figure 2-7) following the extraction (2-8) and stripping reaction (2-9), respectively [2_9]. The carrier is deprotonated during complexation. Concentrated acid is used as stripping agent. The transport of metal cations is coupled to the transport of protons in the opposite direction (see Figure 2-8).

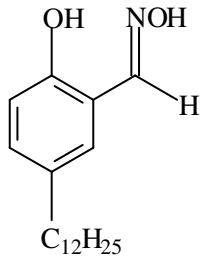


Figure 2-7. Structure of LIX 860-I

Extraction reaction:

$$Cu^{2+}{}_a + 2HL_o \rightarrow CuL_{2o} + 2H^+{}_a \qquad (2\text{-}8)$$

Stripping reaction:

$$CuL_{2o} + 2H^+{}_a \rightarrow Cu^{2+}{}_a + 2HL_o \qquad (2\text{-}9)$$

where HL is an acidic carrier molecule.

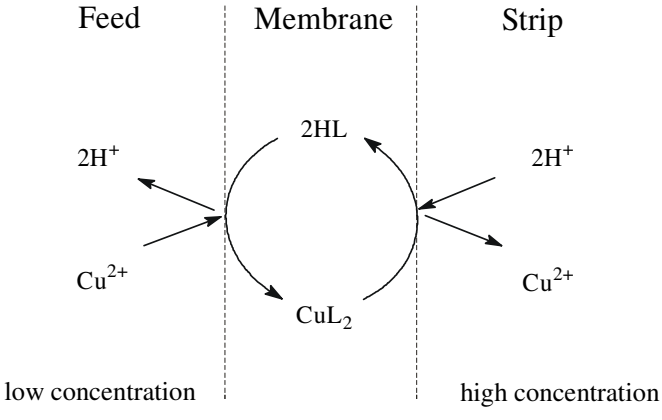


Figure 2-8. Extraction of Cu(II) from waste water

As shown in Figure 2-8, the Cu(II) ion reacts at the aqueous/membrane interface with the extractant HL, present in the liquid membrane, to form the complex CuL_2. During complexation, 2 protons are released into the aqueous feed phase. The copper complex

diffuses through the membrane phase towards the interface between the membrane and receiving or strip phase (acidic phase). Here, the stripping reaction (2-9) takes place. During decomplexation, the protons of the strip solution are exchanged for the copper ions and are accepted by the extractant in the membrane phase. The concentrated acid drives the stripping reaction as shown in Equation (2-9) to the right and maintains a low concentration of the copper complex at the interface adjacent to the strip phase, resulting in a high driving force in terms of the copper complex concentration difference between the feed and strip interfaces and thus a high extraction rate. The driving force of proton transport facilitates the transport of a metal ion against its own concentration gradient between the feed and receiving phases.

2.2. CARRIERS OR EXTRACTANTS

In Supported Liquid Membranes (SLM), an organic carrier solution is held in the pores of a micro-porous membrane by capillary forces. This "liquid membrane" serves as a barrier between the feed and receiving phase (see also Figure 2-1). The choice of the extractant is of primary importance in developing a suitable liquid membrane system for a specific metal ion. The most efficient use of extracting agents requires a sufficiently fast and strong binding for the metal ions to be extracted besides good decomplexation characteristics allowing a total recovery of the metal without loss of ligand [2_10]. The extractants must be highly stable against hydrolysis and a selective complexation is required with no or few affinity for alkali or alkaline earth ions, whose concentrations are usually high in natural waters and soils [2_10]. High selectivities can be obtained when the extractant is very specific to one single metal ion. In fact, every specific solute needs its own specific extractant, which makes this selection very important but also very difficult. Much information about carrier selection can be obtained from liquid-liquid extraction experiments [2_10].

According to their functional groups, the different types of extractants are generally divided into three classes: neutral, basic and acidic extractants [2_6]. In the succeeding paragraphs, these three classes of carriers will be discussed. However, it must be noticed that the mentioned extractants are only a non-limitative list of examples. Finally, the usefulness of mixed extractant systems in liquid membrane processes will be discussed. Sometimes, mixtures of extractants are applied in the extraction process because of their synergistic relationship. In fact, synergism can be defined as a cooperation of two extractant molecules to transfer metal cations from an aqueous medium into an organic phase, in order to satisfy

the solvatation and coordination sites of the metal ion [2_11]. One extractant complexes the metal ion and neutralizes the charge while another extractant may serve to replace water molecules or to occupy free coordination sites [2_11].

2.2.1. Neutral extractants

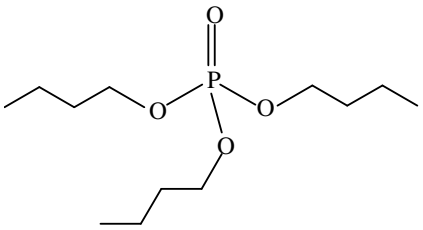
Neutral extractants often extract uncharged metal complexes or cations together with anions in order to maintain the electrical neutrality in the membrane phase. The metal species are coordinated with two different types of ligands, a water-soluble anion and an organic-soluble electron-donating functional group. Two main groups can be distinguished within the class of the neutral extractants: organo-phosphoryl compounds, such as tri-n-butylphosphate (TBP, distributed by VWR International), tri-n-butylphosphine oxide (TBPO, distributed by VWR International) and tri-n-octylphosphine oxide (TOPO, CYTEC), and macrocylic ligands, which include crown ethers and their derivatives (see Figure 2-9) [2_6].

The first class of neutral extractants or organo-phosphoryl compounds are used for the separation of actinides and lanthanides and are useful for the recovery of uranium and plutonium in the spent fuel reprocessing of nuclear plants. The following classification can be made according to their ability of solvatation: trialkylphosphine oxides > trialkylphosphonates > ketones > alcohols > ethers [2_6, 2_12]. The most important commercial application of TOPO in metal extraction is its use in combination with D2EHPA (di(2-ethylhexyl)phosphoric acid) for the extraction of UO_2^{2+} from wet process phosphoric acid.

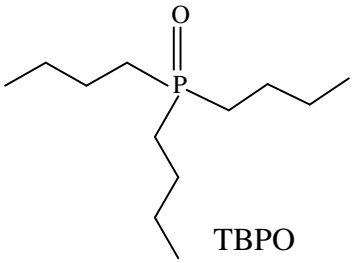
The second class of neutral extractants, the macrocyclic ligands, contains hetero atoms capable of forming electron-rich interior cavities. In many cases, they have the remarkable property of selectively complexing particular ions [2_6]. On the one hand, the macrocyclic effect results in increased stabilities of the complexes and on the other hand, the ratio of the diameter of the cation to that of the cavity provides an additional criterion for selectivity [2_13]. K^+ can be transported selectively compared to other monovalent cations and Pb^{2+} compared to other divalent cations with dibenzo-18-crown-6 as extractant in a liquid membrane [2_14]. In general, oxygen macrocycles such as crown ethers are effective for the extraction of alkali and alkaline earth metal salts and the nitrogen analogue macrocycles are effective for transition metal salts [2_10]. At present, the initial costs of the macrocylic compounds are still very high and in some cases, their solubility in aqueous phases prevents

them from being suitable for large-scale processes [2_10]. Modification of these macrocycles with long-chain aliphatic compounds makes them more applicable in liquid membrane processes. Compared to solvent extraction, the consumption of these expensive compounds in a Supported Liquid Membrane is much lower. This makes these extractants quite competitive in a liquid membrane process for the separation of precious metals. One of the important tasks of chemists is to develop economical methods of synthesizing these compounds with the necessary phase distribution and metal coordination properties [2_6].

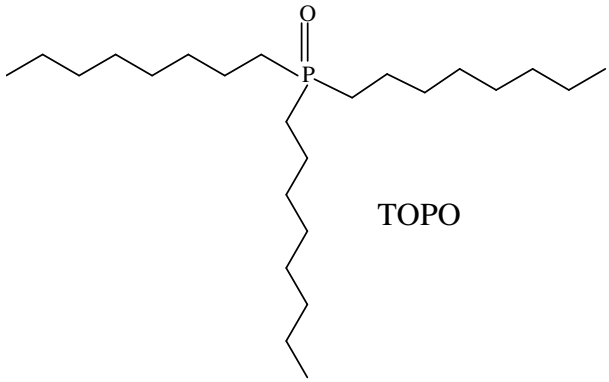
Organo-phosphoryl compounds



TBP

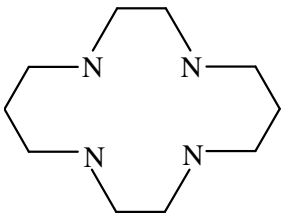


TBPO

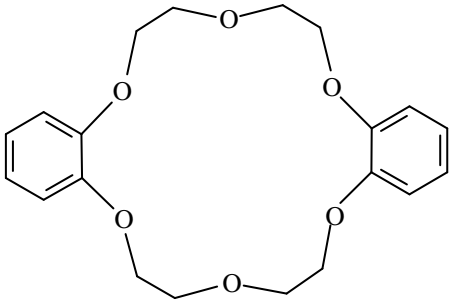


TOPO

Macrocyclic ligands



1,4,8,11-tetraazacyclotetradecane



dibenzo-18-crown-6

Figure 2-9. Structures of neutral extractant molecules

For liquid membranes with neutral carriers, the concentration gradient driving force across the membrane phase must be accomplished by incorporating strong metal complexing agents in the strip phase. Coupled transport is however also possible with macrocylic carriers (see Figure 2-6).

2.2.2. Basic extractants

Basic extraction reagents can extract any metal capable of forming anionic complexes in aqueous solutions. In aqueous solutions, many metal ions can form a variety of anionic complexes with sulphate, cyanate, thiocyanate, cyanide, chloride and a number of other anionic ligands. Examples of anionic metal complexes that commonly exist in solutions in hydrometallurgical and electroplating processes are: $Cd(CN)_4^{2-}$, $AuCl_4^-$, etc [2_6].

The extraction with basic carriers is based on the principle of ion association. Examples are tertiary amines such as tri-n-octylamine (TNOA, distributed by VWR International) and Alamine 336 (Cognis), which consists of a mixture of tertiary amines with alkyl chains varying from C8 to C10, or quaternary alkyl ammonium salts such as Aliquat 336 (Cognis), which consists of quaternary ammonium compounds with alkyl chains varying from C8 to C10 [2_6]. Their structures are shown in Figure 2-10.

In the case of fully substituted quaternary ammonium compounds, the carrier reacts as an anion exchanger forming an ion-pair with a metal-anion complex from the aqueous phase, e.g. the dichromate extraction by quaternary ammonium salts [2_6, 2_15]. The dichromate extraction by quaternary ammonium salts follows the counter-coupled transport mechanism. This means that the permeation of the metal-anion complex of the aqueous phase is transported in the direction opposite to the anions of the strip phase [2_6]. The transport mechanism is shown in Figure 2-11 as well as in the extraction and stripping reaction (2-10) and (2-11), respectively.

Extraction reaction:

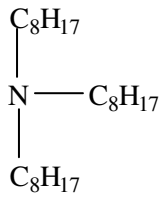
$$2H^+_a + Cr_2O_7^{2-}{}_a + \left(R_3NH\right)_2Cl_2{}_o \rightarrow (R_3NH)_2Cr_2O_7{}_o + 2H^+_a + 2Cl^-_a \qquad (2\text{-}10)$$

Stripping reaction:

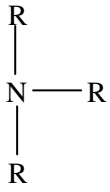
$$(R_3NH)_2Cr_2O_7{}_o + 2H^+_a + 2Cl^-_a \rightarrow 2H^+_a + Cr_2O_7^{2-}{}_a + \left(R_3NH\right)_2Cl_2{}_o \qquad (2\text{-}11)$$

where $\left(R_3NH\right)_2Cl_2$ is the dimer tertiary ammonium salt.

Tertiary amines

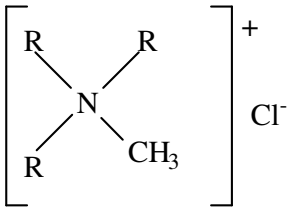


TNOA



Alamine 336
[consists of a mixture of tertiary amines with alkyl chains (R) varying from C8 to C10]

Quaternary alkylammonium salt



Aliquat 336
[consists of a mixture of quaternary ammonium compounds with alkyl chains (R) varying from C8 to C10]

Figure 2-10. Structures of some basic extractant molecules

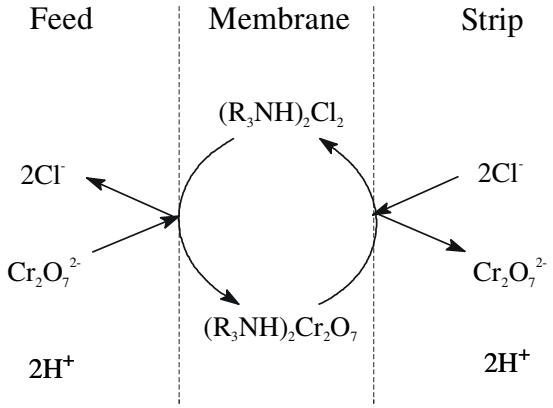


Figure 2-11. Dichromate extraction following the counter-coupled transport mechanism [2_6]

In the case of amines, the carrier must be protonated to react with the metal anion complex or may react directly with a protonated metal-anion complex, e.g. the dichromate extraction with tertiary amines [2_6, 2_15]. The dichromate extraction with a tertiary amine follows the co-coupled transport mechanism. The dichromate extraction with a tertiary amine was already discussed in paragraph 2.1.2.2.

The commercial tertiary amine, Alamine 336, is widely used as extractant for acidic brines, while the commercial quaternary ammonium salt Aliquat 336 is not pH dependent [2_12]. As a result, Aliquat type reagents may successfully treat some basic metal leach solutions without any pH adjustment.

The choice of the stripping reagent depends on the recovery process, but in general, basic stripping agents that deprotonate the amine show the best stripping characteristics [2_12]. Amine type reagents can be stripped with a wide variety of inorganic salt solutions such as NaCl, Na_2CO_3 and $(NH_4)_2SO_4$. The biggest disadvantage of using an Aliquat reagent is that these reagents will not deprotonate. Therefore stripping is usually more difficult than with the parent amine type reagent [2_12].

2.2.3. Acidic extractants

To extract a cation from an aqueous solution, it must be combined with an anion to form an uncharged complex. Acidic extractants are very effective for the separation of cations by exchanging their protons for the cations. Commonly used acidic extractants can be classified into three main categories [2_6, 2_15]:

1) Chelating extractants
2) Alkylphosphorous compounds
3) Ionisable crown ethers

The transport of a cation across a membrane by an acidic extractant follows the counter-current transport mechanism (see Figure 2-8), in which hydrogen ions are used to generate the driving force for solute permeation across the membrane.

2.2.3.1. Chelating extractants

Compounds containing a group with an easily dissociating proton near an atom with a free electron pair are called metal chelating systems [2_16]. Chelation refers to “claw”, which is a graphic description of the way in which the organic extractant binds the metal ion

[2_16]. In general, the coordination complex of the chelating extractant with metal cations is very specific. Chelating extractants can be classified into two groups [2_6, 2_15]:

- hydroxyoximes
  - α-acyloin oximes or aliphatic hydroxyketone oximes such as 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63, Cognis)
  - 2-hydroxybenzaldehyde oxime derivatives such as 5-dodecylsalicylaldoxime (LIX 860-I, Cognis)
  - aliphatic-aromatic hydroxyoximes such as 2-hydroxy-5-nonylacetophenone oxime (LIX 84-I, Cognis)
- β-diketones such as benzoylacetone (distributed by VWR International)

Their structures are depicted in Figure 2-12.

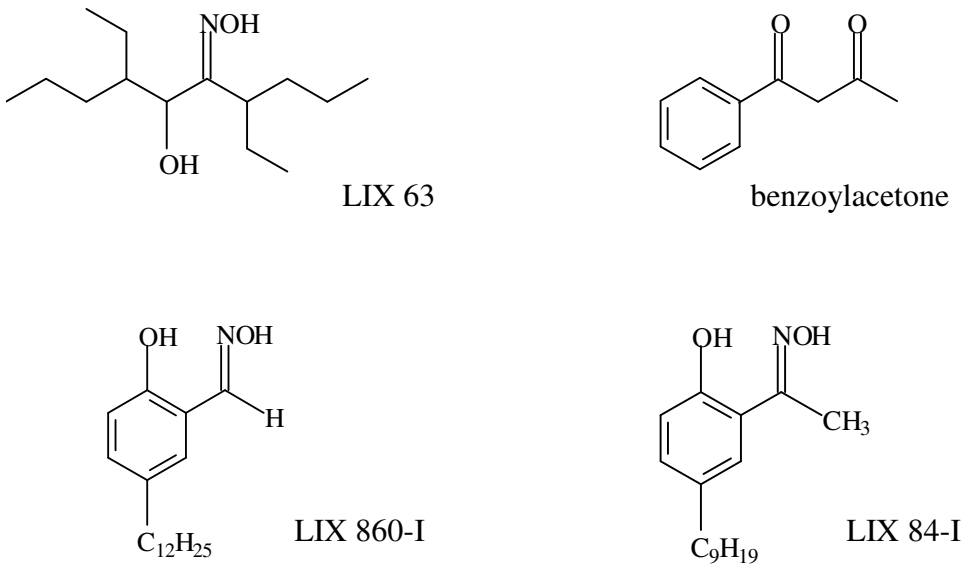


Figure 2-12. Structures of chelating extractant molecules

Hydroxyoximes are the most commonly used chelating agents. Hydroxyoximes reveal two chemically active groups: a hydroxyl group and an oximino group with a free electron pair on the nitrogen atom. The acidity of the hydroxyl group is higher than that of the oximino group. As a result, in normal extraction systems, only the dissociation of the hydroxyl group can be considered and that is why these extractants can be abbreviated as HL [2_16].

Aromatic (e.g. LIX 860-I) as well as aliphatic (e.g. LIX 63) hydroxyoximes can be used in extraction processes [2_16]. Two various types of bonds exist in the chelate: the chelating ligand-metal bond and π donor metal-ligand bond. A change of the electron density of the nitrogen atom of the ligand changes the relative strength of these bonds.

The aromatic hydroxyoximes can be divided into two distinct classes, based on their structure and properties:

1) Ketoximes, such as LIX 84-I
2) Salicylaldoximes, such as LIX 860-I

These phenolic oximes find extensive use in industry, mainly as extractants for copper, but also as anticorrosives in protective coatings [2_16]. Ketoximes, which are normally copper extractants of moderate strength, were the first hydroxyoxime reagents to be used commercially for the extraction of copper from dilute sulfuric acid leach liquor [2_12]. The most outstanding feature of the ketoximes is their good physical performance under a wide variety of conditions. The salicylaldoximes were developed to overcome the shortcomings of the ketoximes. These extractants can be characterised by their high extractive strength and rapid copper transfer kinetics [2_12]. A general comparison of their properties as well as of their mixtures is given in Table 2-1 [2_17].

Table 2-1. General comparison of the properties of ketoximes, aldoximes and their mixtures [2_17]

Property	Ketoxime	Aldoxime	Mixtures
Extractive strength	Moderate	Strong	Customized
Stripping	Good	Reasonable	Customized
Cu/Fe selectivity	Excellent	Excellent	Excellent
Copper kinetics	Good	Fast	Fast
Phase separation	Fast	Fast	Fast
Stability	Excellent	Good	Good

The strength and selectivity of the complex formation with copper have been assumed to arise from a very favourable goodness-of-fit for the bonding cavity in the ligands, which is defined by hydrogen bonding between two bidentate units (see Figure 2-13) [2_18].

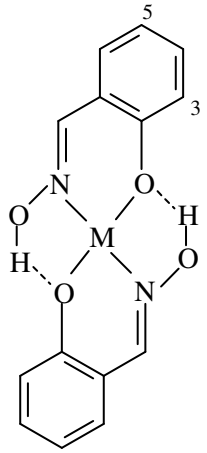


Figure 2-13. Hydrogen bonding in 2:1 complexes between phenolic oxime units and the metal ion [2_18]

For aromatic hydroxyoximes with the same substituents in the aromatic ring, the acidity decreases in the order: 2-hydroxybenzaldehyde oxime derivatives > aliphatic-aromatic hydroxyoximes > 2-hydroxybenzophenone oxime derivatives [2_16]. Copper-ligand stability constants and the extraction ability of hydroxyoxime structural types also decrease in the same order [2_16]. They are, however, of similar order. Nonetheless, these relatively small differences in the stability constants are sufficiently significant to observe a different extraction behaviour for the hydroxyoximes in actual extraction systems [2_16].

If a nucleophilic substituent is present in position 3 or 5 in the aromatic ring (e.g. an alkyl group, see Figure 2-13), which increases the electron density of the phenolic oxygen, then the acidity of the hydroxyoximes decreases. The decrease is the result of an induction effect and the hyper-conjugation of the alkyl groups [2_16]. Nucleophilic substituents located in position 3 or 5 of the aromatic ring usually cause an increase of the complex stability. In the case of an alkyl group as substituent located in position 5 of the aromatic ring, the copper-ligand stability constants increase with an increase of the length of the alkyl group [2_16].

The introduction of an electrophilic substituent into the aromatic ring (e.g. a halogen or nitro group) increases the phenolic group acidity [2_16]. The location of the oximino group however has a much stronger effect on the acidity of the phenolic group than the type of substituents bonded with the aromatic skeleton [2_16]. Furthermore, electrophilic substituents usually cause a decrease of the stability of the complex [2_16].

The extraction with chelating agents follows the counter-current transport mechanism, which is explained in paragraph 2.1.2.3 for the metal ion copper(II). One of the important parameters controlling the equilibrium of the extraction reaction is the acid content of the aqueous phase. A graphic representation of this behaviour is referred to as a pH isotherm. Some typical pH isotherms for LIX 84-I are shown in Figure 2-14 [2_12].

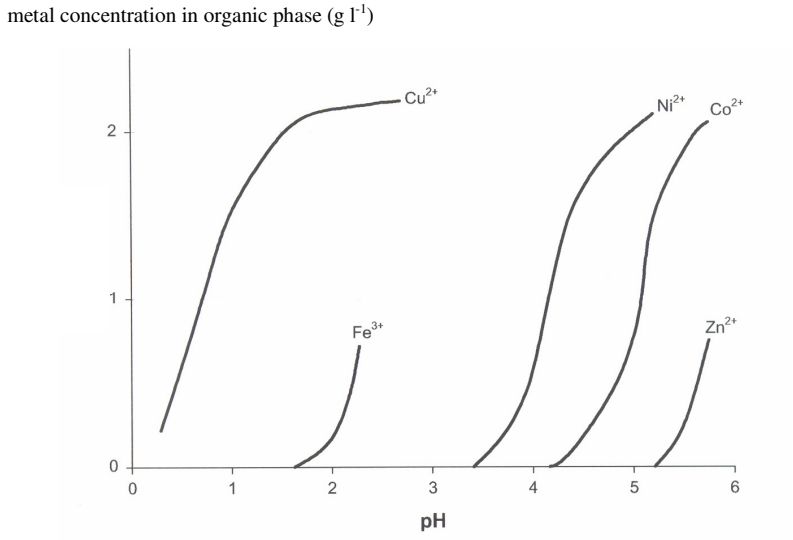


Figure 2-14. pH-isotherms of LIX 84-I [2_12]

The pH isotherms can be used to predict the extraction characteristics of the reagent with respect to the metals shown under a variety of conditions. For example, at pH 2.0, copper(II) is strongly extracted, ferric ion is slightly extracted, while nickel(II) and cobalt(II) are not extracted. However, at pH 5.0, all four of these metals would be strongly extracted. This fact is however not important for iron(III) since it is only slightly soluble at pH 5.0 [2_12].

The selectivity depends not only upon the type of extractant, but also upon the type of diluent and the composition of the aqueous phase [2_16].

2.2.3.2. Alkylphosphorous compounds

Alkylphosphorous extraction agents are less selective compared to the chelating extractants. On the other hand, they are less expensive and their metal complexes are more

soluble in organic solvents than metal chelates [2_12]. Therefore, they are also widely used in hydrometallurgical processes. Reagents belonging to this class are [2_6, 2_12, 2_15]:

- organophosphoric acids such as di(2-ethylhexyl)phosphoric acid (D2EHPA, distributed by VWR International) and dibutylphosphoric acid (DBP, Lanxess)
- organophosphonic acids such as mono(2-ethylhexyl)ester of 2-ethylhexylphosphonic acid (PC-88A, Daihachi Chemical Industry)
- organophosphinic acids such as di(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272, CYTEC)
- thiophosphoric acids such as di(2-ethylhexyl)dithiophosphoric acid (DTPA, Hoechst)
- thiophosphinic acids such as di(2,4,4-trimethylpentyl)monothiophosphinic acid (CYANEX 302, CYTEC) and di(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301, CYTEC)

Their structures are depicted in Figure 2-15.

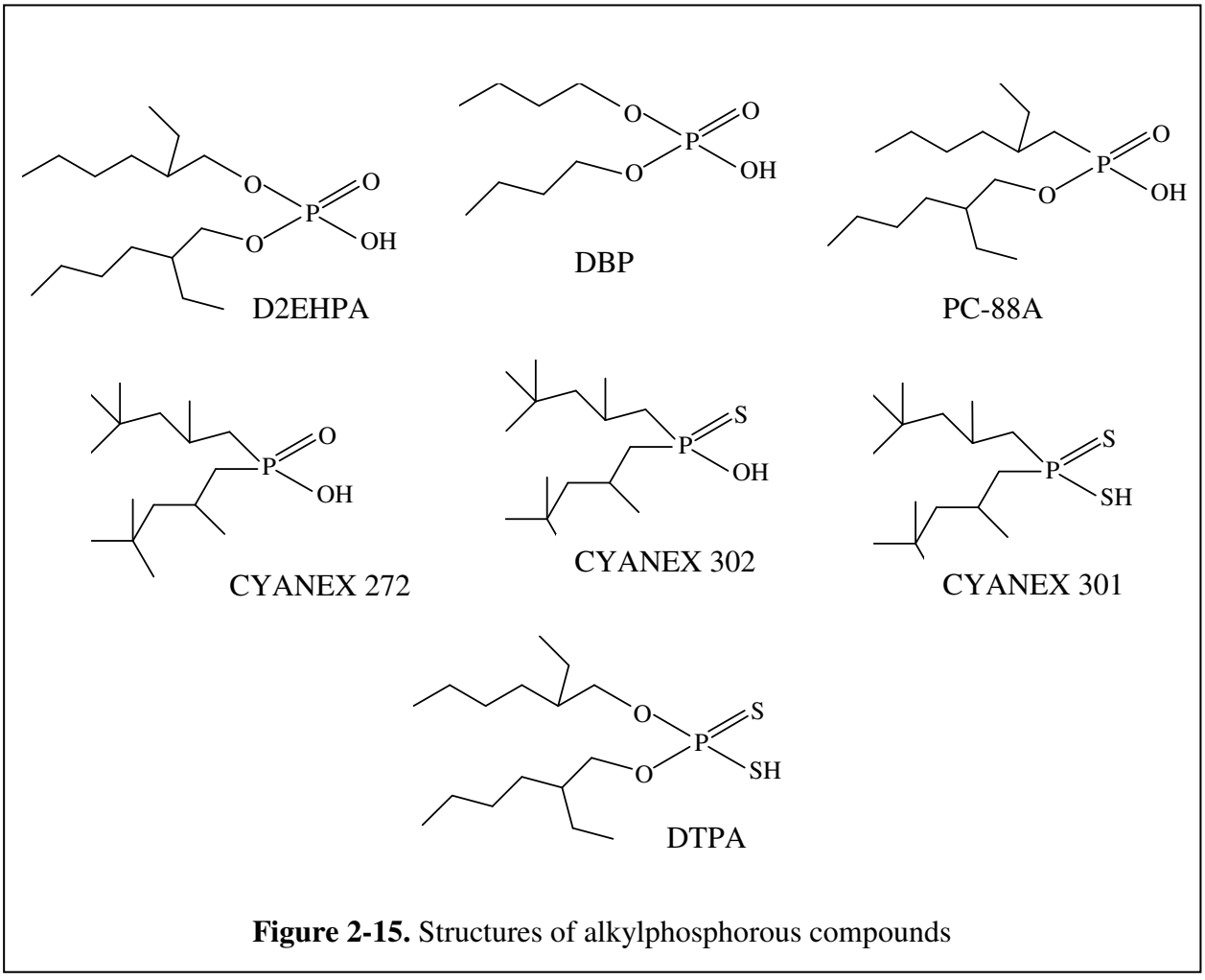


Figure 2-15. Structures of alkylphosphorous compounds

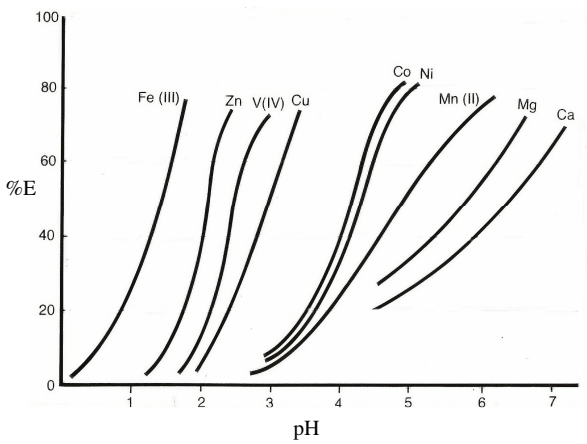
The chemistry of the alkylphosphorous compounds has characteristics which resemble the chelating extractants, but also characteristics which are similar to neutral or solvating extractants [2_12]. One of the characteristics of the extraction behaviour of alkylphosphorous extractants is their strong affinity for iron over other metal ions [2_12].

The organophosphoric acid, D2EHPA, is a very efficient and versatile extraction agent in liquid-liquid extraction processes for the purification, enrichment, separation and recovery of metal salts e.g. rare earths, extraction of UO_2^{2+}, separation of cobalt and nickel and the extraction of zinc, vanadium and beryllium [2_19]. D2EHPA replaces the carboxylic acids in metal extraction because of smaller extractant losses, higher metal loadings and faster equilibrium rates [2_20].

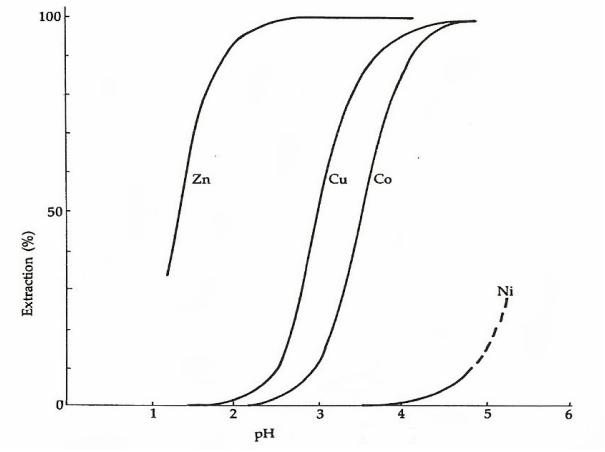
The subsequent development of phosphonic and phosphinic extractants, in particular PC-88A and CYANEX 272, led to drastic improvements in cobalt-nickel separation factors in the order: phosphoric < phosphonic < phosphinic acid (see Figure 2-16). The selectivity for the separation of cobalt from nickel increases when the alkoxy oxygens attached to the phosphorous atom are progressively removed. The progressive removal of the alkoxy oxygens shortens the distance between the alkyl chains and the phosphoryl group. This shorter distance reduces the stability of the nickel complexes because of steric hindrance [2_23]. On the other hand, the stability of the cobalt complexes does not change along the sequence phosphoric, phosphonic, phosphinic acid [2_23]. The stability of both complexes decreases however by increasing the branching of the alkyl chains [2_23].

CYANEX 272 offers another important advantage compared to D2EHPA and PC-88A because it is the only one which extracts cobalt in preference to calcium (this is however not correctly depicted in the pH isotherms of CYANEX 272 in Figure 2-16). This property can minimize or eliminate problems, which are associated with calcium extraction [2_24]. Due to its superior Co/Ni selectivity, CYANEX 272 was quickly adopted in Ni/Co refineries. The first plant to use this reagent was started in 1985 and by 1990 there were three more plants, including two major Co-refineries in Europe [2_25].

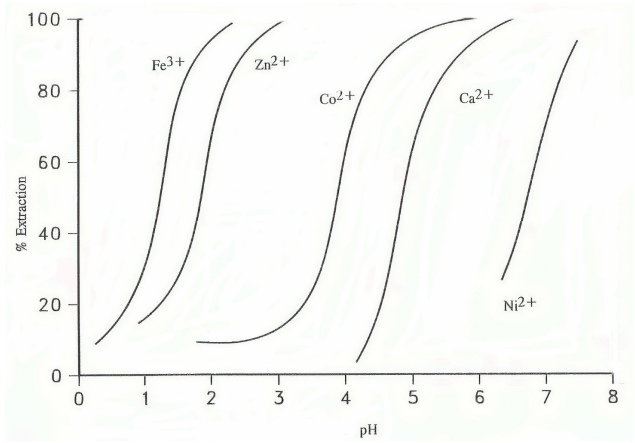
Although CYANEX 272 is selective for cobalt in the presence of nickel, a wide variety of other cations can also be extracted depending upon the pH of the solution as shown in the pH-isotherms of Figure 2-16.



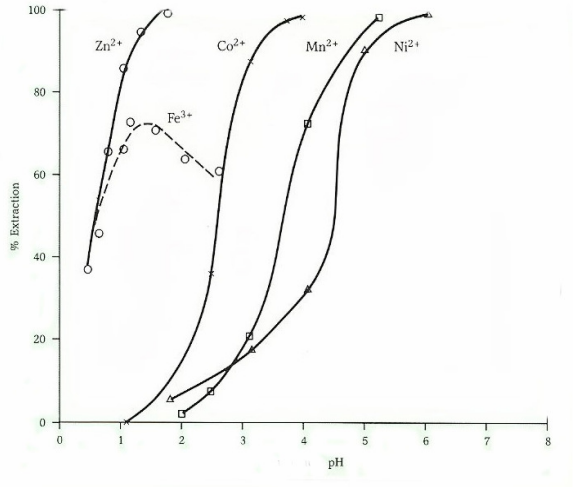
D2EHPA [2_12]



PC-88A [2_21]



CYANEX 272 [2_22]



CYANEX 302 [2_22]

Figure 2-16. pH-isotherms of some organophosphorous compounds

The thiosubstituted organophosphinic ligands, CYANEX 302 and CYANEX 301, were developed by CYTEC in the late 1980s as extractants for the selective extraction of zinc from effluent streams containing calcium or magnesium, such as those generated in the manufacture of rayon by the viscose process [2_25]. Although similar in many respects to CYANEX 272, the progressive replacement of oxygens with sulfur results in reagents with a very different extraction strength and selectivity for base metals [2_25].

According to the Hard-Soft Acid-Base (HSAB) principle, the complexation of a soft Lewis acid, such as Ni(II), Cu(II), Co(II) or Zn(II), with a soft Lewis base should occur with high selectivity. The donor atoms of the most common Lewis bases have electronegativities

increasing in the order S < Br < N, Cl < O < F. Sulfur substitution of organophosphorous reagents should therefore be beneficial for the extraction of these metal ions [2_26]. The significantly lower electronegativity of sulfur renders it more polarizable than oxygen. Electrons are more readily shared in a metal-sulfur bond than in a metal-oxygen bond, introducing a greater degree of covalency and increasing the strength of the bond [2_27].

The effect of sulfur on the pK_a of the extractant is particularly important since it determines the performance characteristics of these extractants [2_26]. Table 2-2 reports the approximate pK_a values of the organophosphinic reagents [2_27].

Table 2-2. pK_a values of the organophosphinic extractants [2_27]

Extractant type	pK_a
CYANEX 272	6.37
CYANEX 302	5.63
CYANEX 301	2.61

The fundamental difference between CYANEX 302 and CYANEX 272 is that metal separations can be carried out at a lower pH (see also Figure 2-16). This is also true for CYANEX 301, a dialkyldithiophosphinic acid extractant and a much stronger acid compared to CYANEX 272 due to its sulfur substitution [2_28]. CYANEX 301 is capable of extracting many metal ions at low pH (< 2). This extractant does not discriminate between heavy metals in this pH range. However, a high degree of selectivity is observed in the extraction of heavy metal ions towards the alkaline earth metals [2_28]. Dithiophosphoric acids are also commercially available. However, acids of this type do not exhibit the high selectivity for zinc versus calcium, which is associated with CYANEX 301 [2_28]. CYANEX 301 may also be useful for removing small quantities of heavy metals from acid process streams where pH adjustment is not economical [2_24]. However, instability problems limit the usefulness of the thiosubstituted organophosphinic reagents [2_27]. The extraction of copper(II) and iron(III) can be accompanied with the reduction of the metal ion towards copper(I) and iron(II), respectively, and result in the oxidation of the ligands to the disulfide, e.g. $R_2P(S)\text{-}S\text{-}S\text{-}(S)PR_2$ in the case of CYANEX 301 [2_27].

2.2.3.3. Ionisable crown ethers

Attachment of a side arm with potential metal ion binding sites to a crown ether gives a lariat ether. Proton-ionisable lariat ethers are crown ethers with a pendant acidic group as side arm (e.g. carboxylic acid, phosphonic acid and phosphonic acid monoalkyl ester) (see Figure 2-17). Compared with neutral crown ethers, proton-ionisable lariat ethers have an important advantage because the transport of a metal ion through the membrane does not require concomitant transport of an aqueous phase anion [2_29].

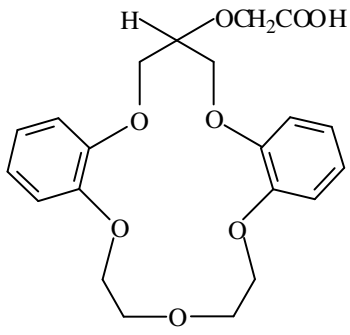


Figure 2-17. Structure of dibenzo-16-crown-5-oxyacetic acid

In fact, the molecule becomes both a cation exchanger and a chelator. Dibenzo-crown ethers with pendant carboxylic acid and hydroxamic acid groups in their side arms have been shown to be efficient ligands for the solvent extraction of alkali metal, alkaline earth metal and lanthanide ions [2_30]. The selectivity and pH range for extraction are influenced by the structure of the ligand. Ionisable crown ethers are mainly the subject of numerous fundamental research studies: e.g. the availability of fluorine-containing lariat ether carboxylic acids encouraged the investigation of their behaviour as lanthanide ion extractants [2_30].

2.2.4. Mixtures of extractants

In the previous paragraphs, the extraction behaviour of the different classes of extractants has been discussed. However, these extractants are not always applied independently in the organic liquid membrane. Sometimes, mixtures of extractants are used in the extraction process because of their synergistic relationship. In fact, synergism can be

defined as a cooperation of two extractant molecules to transfer metal cations from an aqueous medium into an organic phase, in order to satisfy the solvatation and coordination sites of the metal ion [2_11]. One extractant complexes the metal ion and neutralizes the charge while another extractant may replace water molecules or may occupy free coordination sites [2_11]. In this way, a mixture of two extractants produces an extraction percentage which is higher than the sum of the extraction percentages obtained with each extractant independently [2_11].

Among the different extractant combinations in synergistic mixtures, mixtures of acidic carriers and oximes have been used extensively, whereas combinations of two acidic extractants are less common [2_11]. One of the first examples consisted of mixtures of the aliphatic hydroxyoxime LIX 63 and D2EHPA for the separation of copper and cobalt from nickel in sulphate media [2_11]. The Canadian company Eldorado Nuclear Ltd. has patented this process, which was operated on a pilot plant scale but has not been further developed. Pilot plant status has also been achieved by a process for the separation of cobalt from nickel using the same reagents at higher concentrations for which patents have been granted to Metallurgie Hoboken, Overpelt in Belgium [2_31, 2_32]. Later, the synergistic extraction of nickel with mixtures of LIX 63 and several carboxylic acids and organophosphoric acids was studied, indicating an increase in the synergistic effect with the acidity constant of the extractants [2_33-2_34]. In the LIX 63-carboxylic acid systems, synergism is considered to result from the formation of a mixed ligand complex having a greater solubility in the solvent phase than either the metal-LIX or metal-carboxylate species [2_33]. The application of such mixed-extractant systems to commercial operations has not yet been made [2_33]. They suffer from problems such as poor stripping characteristics or high solubility of carboxylic acids in the aqueous phase [2_33].

In general, synergism has been shown to occur in many mixed solvent systems, but the actual mechanisms involved are still largely unresolved. The addition of a second carrier may exhibit a deleterious influence upon the extraction equilibrium when the second carrier can interact with the extractant through the formation of hydrogen bonds [2_34]. Such interactions therefore compete with the metal extraction reaction. On the other hand, interaction with the extracted metal complex can occur for instance by replacement of the coordinated neutral extractant molecules and/or water molecules or by transformation of the coordination geometry as also described in the definition of synergism [2_11]. These changes in coordination properties may enhance the complex solubility in the organic phase and change the extraction and/or stripping behaviour for certain species and its selectivity.

In literature, D2EHPA/LIX 63 and D2EHPA/2-ethylhexanal oxime (EHO) systems showed remarkable synergistic effects produced by the presence of nitrogen-donor ligands in extraction equilibria [2_34-2_35]. In fact, a considerable decrease in the pH values of 50% metal extraction ($pH_{0.5}$) was found for cobalt and nickel [2_34-2_35]. In Figure 2-18, the pH shifts are shown for cobalt and nickel extraction with the D2EHPA/EHO and D2EHPA/LIX 63 system [2_35].

The shifts towards lower pH values enable these metals to be extracted under acidic conditions (pH 0-3) [2_35]. The addition of EHO also causes marked synergistic effects during the extraction of other base metals. The extent of the synergistic effect lies in the order: Cr < Mn < Fe < Co < Cu < V < Ni, which also represents, with the exception of Cr^{2+}, the order of increasing ligand-field stabilisation of octahedral complexes over the corresponding tetrahedral complexes.

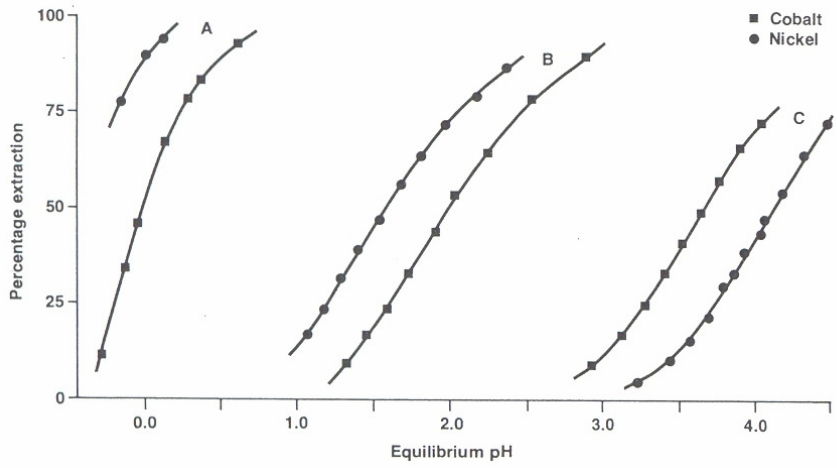


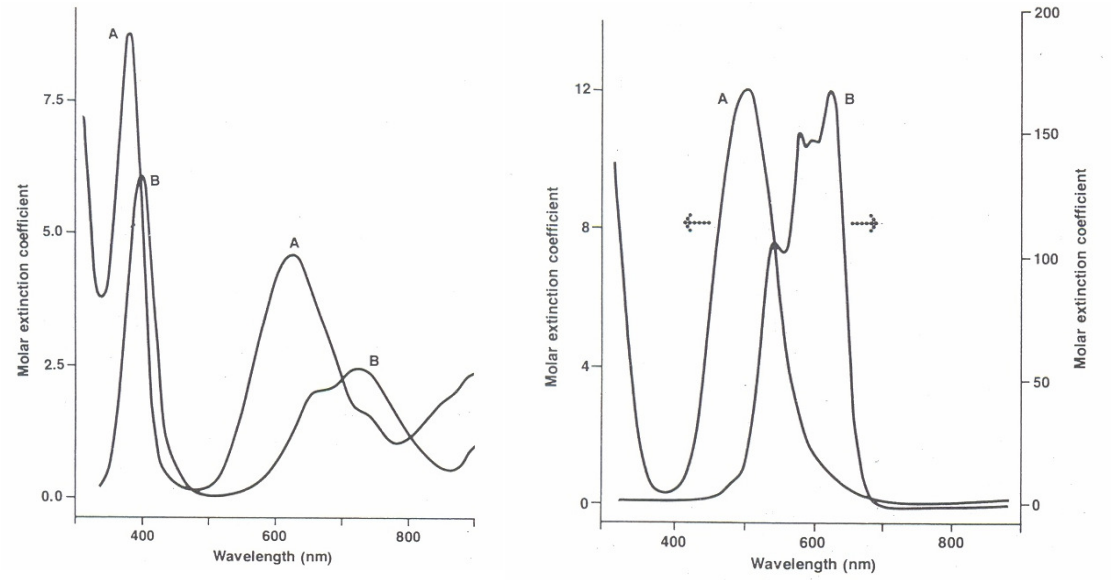
Figure 2-18. Extraction of cobalt and nickel by mixtures of D2EHPA and oximes in xylene [2_35].

Organic phases: A. 0.50 M D2EHPA-0.50 M LIX 63; B. 0.50 M D2EHPA-0.50 M EHO; C. 0.50 M D2EHPA. Aqueous phase: 0.10 M metal nitrate in 1.00 M NH_4NO_3.

The synergistic effect of EHO on the extraction of the divalent transition metals by D2EHPA reveals its role in the formation of mixed-ligand octahedral complexes [2_35]. The changes in electronic spectra of the nickel and cobalt complexes are shown in Figure 2-19. The spectrum of the nickel complex shows a displacement towards higher excitation energies due to the incorporation of nitrogen-donor ligands into the metal complex. The apple-green

colour of the nickel-D2EHPA complex changes to turquoise blue in the mixed complex [2_35]. In the case of cobalt, the deep blue tetrahedral D2EHPA complex is transformed to a pink octahedral one [2_35].

The absence of significant synergistic effects among the divalent non-transition metals (e.g. calcium and magnesium) can be ascribed to the preference of these cations towards oxygen-donor ligands. Also no marked synergistic effects were found for the trivalent ions studied, such as Fe(III) and Cr(III) [2_35].



Nickel Cobalt

Figure 2-19. Electronic spectra of D2EHPA-EHO extracts in xylene [2_35].
A. 0.10 M metal and 0.50 M D2EHPA-0.50 M EHO
B. 0.10 M metal and 0.50 M D2EHPA

The influence of various types of non-chelating oximes on the extraction of nickel and cobalt by 0.50 M solutions of D2EHPA in xylene are shown in Figure 2-20 [2_35].

Oximes of different structures produce different synergistic effects. The main factor in determining the extent of the synergistic effect is the steric hindrance of the oxime function [2_35]. Molecular models have shown that in the mixed-ligand complex, the substituent hydrocarbon groups on the oxime are brought into close proximity towards the organophosphoric acid extractants [2_35]. Severe steric hindrance occurs unless the substituent contains at least one α-hydrogen. The largest synergistic effects occur with

aliphatic aldoximes of the primary and secondary carbon chain types (RCH_2-CNOH-H) and (R_2CH-CNOH-H), respectively [2_35].

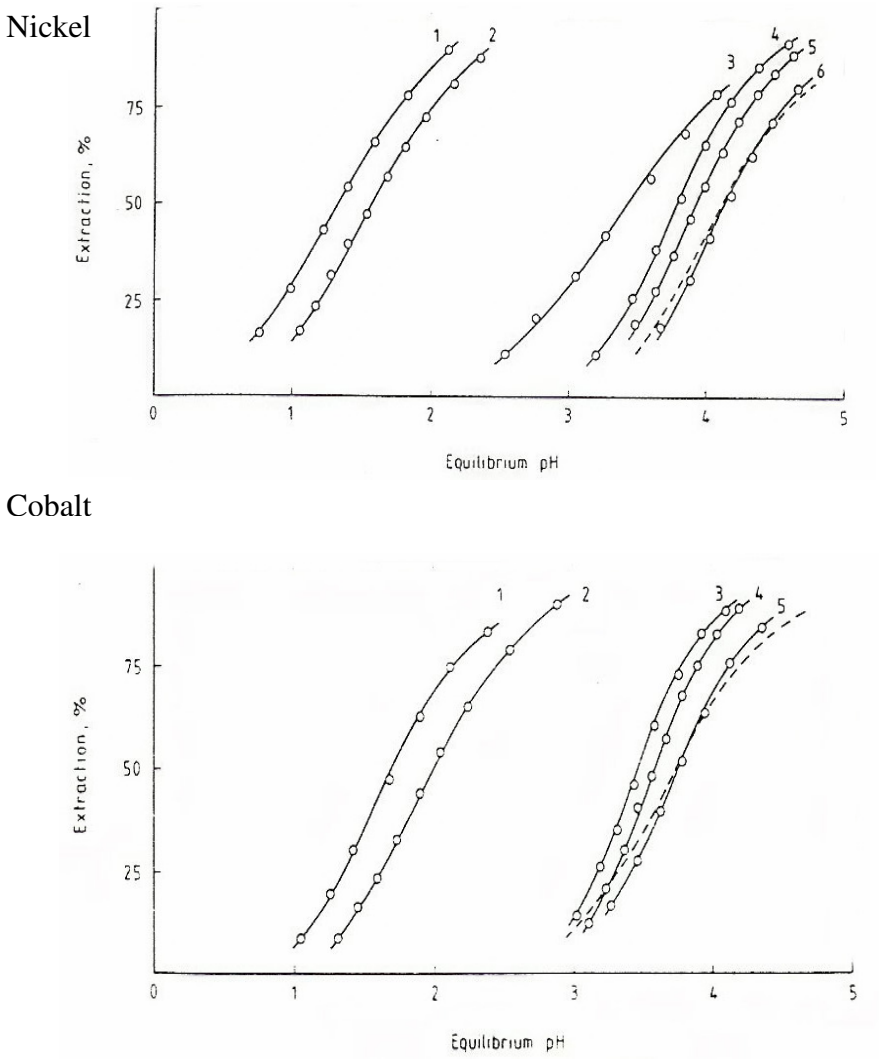


Figure 2-20. Extraction of nickel and cobalt by mixtures of D2EHPA and non-chelating oximes [2_35].

Aqueous phases: 0.10 M metal nitrate in 1.0 M (NH_4, H)NO_3

Organic phases: 0.50 M D2EHPA – 0.50 M oxime in xylene

Oximes: (1) octanal oxime; (2) 2-ethylhexanal oxime; (3) 2,2-dimethylpropanal oxime; (4) octan-2-one oxime; (5) octan-3-one oxime; (6) 2,4-dimethylpentan-3-one oxime.

The dashed line shows the extraction of the metal ion by 0.50 M D2EHPA alone

In literature [2_36], it was indicated however that EHO-D2EHPA mixtures are unsuitable for use in a continuous counter-current solvent extraction process. The acidic strip solutions partially degrade the oxime. Several straight-chain aliphatic oximes were tested for the extraction of nickel [2_36]. The extraction kinetics were similar to those of EHO combined with D2EHPA. Based on stability considerations, decanaloxime (DOX) proved to be the most satisfactory reagent for the extraction of nickel in combination with D2EHPA, although its application to commercial systems is restricted [2_36].

Another extractant system described in literature is based on a mixture of different types of alkylpyridines and carboxylic acids for the extraction of nickel [2_37]. The addition of alkylpyridines produces marked synergistic effects in the extraction of nickel by carboxylic acids, and antagonistic effects in the extraction of calcium, thereby enabling improved separation of these metal ions [2_37].

The examples of extractant mixtures discussed above show that synergism can occur if different types of extractants are combined. In Chapter 3, a study will be made of mixed extractant systems with the aromatic hydroxyoxime LIX 860-I and the organophosphorous acids D2EHPA and CYANEX 301 to investigate if synergistic effects occur during the extraction of copper(II), nickel(II), cobalt(II), iron(II, III) and magnesium(II). Furthermore, Fourier-Transform Infrared analysis as well as UV-VIS absorption spectra will be made of the metal-organic complexes to study the influence of mixed-extractant systems on the configuration of the metal-organic complexes.

2.2.5. Extraction reactions and equilibrium constants

In order to extract and recuperate a specific cationic metal ion M^{n+} from effluent streams, often acidic agents are used in liquid-liquid extraction applications [2_4, 2_9, 2_12, 2_15]. In non-polar diluents, self-association may occur between the acidic extractant molecules, viz. dimerisation of D2EHPA in benzene [2_27, 2_38]. The degree of self-association is strongly dependent upon the nature of the donor atoms [2_27]. In the case of the organophosphinic acids, the degree of self-association decreases in the order: $R_2P(O)O^-$ (CYANEX 272) > $R_2P(S)O^-$ (CYANEX 302) > $R_2P(S)S^-$ (CYANEX 301) [2_27]. Therefore, in the succeeding paragraphs, the extraction reactions and extraction constants will be discussed for monomeric extractant molecules as well as for dimeric ones.

Furthermore, solvatation of the metal-organic complexes can also play a major role in the extraction mechanism and in the configuration of the metal complexes [2_39].

Solvatation can occur by means of water molecules, e.g. nickel(II), with a coordination number of 6, usually tends to retain several water molecules in its coordination sphere [2_39] (see Figure 2-21). Depending on the extraction circumstances, e.g. type of solvent and extractant concentration, these water molecules can be replaced by the solvent, viz. higher alcohols, or by neutral extractant molecules [2_39]. In some cases, viz. cobalt(II)-D2EHPA complexes, the solvatation of the complex with solvent molecules or neutral extractant molecules can result in a rearrangement of the coordination geometry and in an increase of the coordination number [2_39]. The influence of the type of diluent on the extraction performance of the different extractants and the coordination geometry of the metal-organic complexes will be extensively discussed in Chapter 3.

Besides the solvatation processes, also polymerized metal complexes can be formed, as sometimes mentioned in literature [2_40]. It has been shown that solutions of D2EHPA in organic diluents can be highly loaded with bivalent metal cations like copper(II), cobalt(II), nickel(II), etc. [2_16, 2_40]. The anion of D2EHPA acts as a bridge and the polymers are chains consisting of 8-membered rings as can be noticed in Figure 2-21 [2_40].

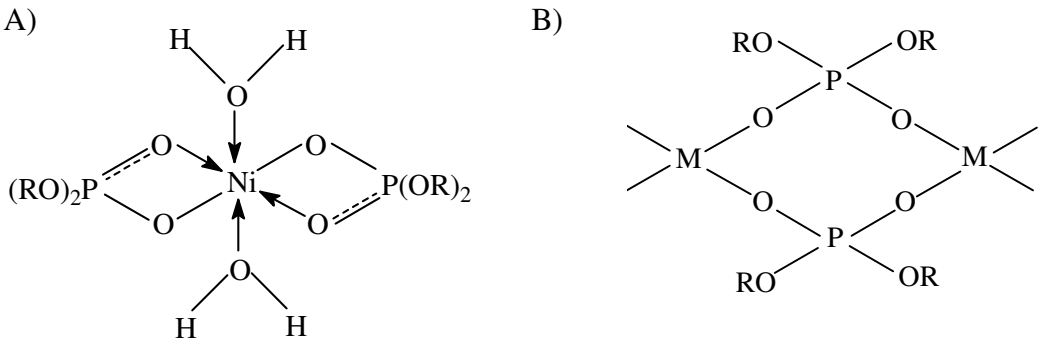


Figure 2-21. Complex solvatation of nickel(II)-D2EHPA complex with water molecules (A) and polymerized metal complexes with D2EHPA (B)

In the succeeding paragraphs, the extraction reactions and extraction constants will be described for monomeric as well as for dimeric extractant molecules. The extraction reactions will also be extended to solvatation and polymerization processes as well as mixed extractant systems. Furthermore, the efficiency of the extraction reaction, expressed as a function of the distribution coefficient or percentage extraction will be discussed.

2.2.5.1. Monomeric extractant molecules

The transport of a cation across a membrane by an acidic extractant follows the counter-coupled transport mechanism (see Figure 2-8), in which hydrogen ions are used to generate the driving force for solute permeation across the membrane.

The extraction by means of a monomeric acidic extractant can be described in its simplest form by the following general reaction:

$$\left[M^{n+}\right]_a + n\left[HL\right]_o \leftrightarrow \left[ML_n\right]_o + n\left[H^+\right]_a \tag{2-12}$$

where the subscripts refer to the organic phase (subscript o) and the aqueous phase (subscript a).

The equilibrium constant K for the extraction reaction of a metal ion M^{n+} with n extractant molecules HL is given by:

$$K = \frac{\left[ML_n\right]_o \left[H^+\right]_a^n}{\left[M^{n+}\right]_a \left[HL\right]_o^n} \tag{2-13}$$

For simplification, concentrations are used instead of activities.

If the solubilities of the free ions in the organic phase are very low, then the concentration of the extractant-metal complex determines the ion concentrations in this phase. This equilibrium can also be expressed using the distribution coefficient k for the metal ion, as shown in Equation (2-14):

$$k_{M^{n+}} \equiv \frac{\left[M^{n+}\right]_o}{\left[M^{n+}\right]_a} = \frac{\left[ML_n\right]_o}{\left[M^{n+}\right]_a} = K\frac{\left[HL\right]_o^n}{\left[H^+\right]_a^n} \tag{2-14}$$

The extraction results can also be expressed as extraction percentages instead of the distribution coefficient k (see Equation (2-15)):

$$\%E = \frac{\left[M^{n+}\right]_o}{\left[M^{n+}\right]_a + \left[M^{n+}\right]_o} x\ 100 \tag{2-15}$$

Complex solvatation with neutral extractant molecules

If the complex solvatation with neutral extractant molecules is also taken into consideration, the extraction reaction (2-12) can be written as:

$$\left[M^{n+}\right]_a + (m+n)\left[HL\right]_o \leftrightarrow \left[ML_n.mHL\right]_o + n\left[H^+\right]_a \tag{2-16}$$

where m denotes the degree of complex solvatation with neutral extractant molecules.

The equilibrium constant K for the extraction reaction of a metal ion M^{n+} with (m+n) extractant molecules HL is then given by:

$$K = \frac{\left[ML_n.mHL\right]_o \left[H^+\right]_a^n}{\left[M^{n+}\right]_a \left[HL\right]_o^{m+n}} \tag{2-17}$$

The distribution coefficient $k_{M^{n+}}$ and percentage extraction can be derived in an analogous way as shown in Equations (2-14) and (2-15), respectively.

Besides the solvatation with neutral extractants, water molecules or sometimes the diluent (e.g. higher alcohols) can also be responsible for the solvatation of the metal-organic complex [2_39]. In these cases, the m neutral extractant molecules in the metal-organic complex have to be replaced by m water or m organic diluent molecules or by a mixture of water and organic diluent molecules.

Complex polymerization

In the case of highly metal loaded organic phases, complex polymerization can occur [2_40]. The extraction reaction (2-12) can then be written as:

$$p\left[M^{n+}\right]_a + np\left[HL\right]_o \leftrightarrow \left[\left(ML_n\right)_p\right]_o + np\left[H^+\right]_a \tag{2-18}$$

where p denotes the degree of complex polymerization.
The extraction constant is given by:

$$K = \frac{\left[\left(ML_n\right)_p\right]_o \left[H^+\right]_a^{np}}{\left[M^{n+}\right]_a^p \left[HL\right]_o^{np}} \tag{2-19}$$

The distribution coefficient $k_{M^{n+}}$ and percentage extraction can be derived in an analogous way as shown in Equations (2-14) and (2-15), respectively.

Complex solvatation with neutral extractant molecules and complex polymerization

If the extraction mechanism involves both complex solvatation with neutral extractant molecules and complex polymerization, the extraction reaction (2-12) can be written as:

$$p\left[M^{n+}\right]_a + \left(m+np\right)\left[HL\right]_o \leftrightarrow \left[\left(ML_n\right)_p.mHL\right]_o + np\left[H^+\right]_a \tag{2-20}$$

where m and p denote respectively the degree of complex solvatation with neutral extractant molecules and the degree of complex polymerization.

The equilibrium constant K for the extraction reaction of a metal ion M^{n+} with (m + np) extractant molecules HL is then given by:

$$K = \frac{\left[(ML_n)_p.mHL\right]_o \left[H^+\right]_a^{np}}{\left[M^{n+}\right]_a^p \left[HL\right]_o^{m+np}} \tag{2-21}$$

The distribution coefficient $k_{M^{n+}}$ and percentage extraction can be derived in an analogous way as shown in Equations (2-14) and (2-15), respectively.

2.2.5.2. Dimeric extractant molecules

Similar extraction reactions can be defined in the case of dimeric extractant molecules. In the case of the extraction of a metal ion with a dimeric acidic carrier and considering that no complex solvatation or polymerization occurs, the extraction reaction can be written as:

$$\left[M^{n+}\right]_a + \left(\frac{n}{2}\right)\left[(HL)_2\right]_o \leftrightarrow \left[ML_n\right]_o + n\left[H^+\right]_a \tag{2-22}$$

The extraction constant K is then given by:

$$K = \frac{\left[ML_n\right]_o \left[H^+\right]_a^n}{\left[M^{n+}\right]_a \left[(HL)_2\right]_o^{n/2}} \tag{2-23}$$

Distribution coefficients and percentage extractions of the extraction processes can be derived in an analogous way as shown in Equations (2-14) and (2-15) for monomeric extractant molecules, respectively.

Complex solvatation with neutral extractant molecules and polymerization

If the self-association (dimerization) of the extractant in the organic phase and the complex polymerization and its solvatation with dimeric extractant molecules are taken under consideration, the extraction reaction can be written as:

$$p\left[M^{n+}\right]_a + \left(\frac{np+m}{2}\right)\left[(HL)_2\right]_o \leftrightarrow \left[(ML_n)_p.mHL\right]_o + np\left[H^+\right]_a \tag{2-24}$$

where m and p denote respectively the degree of complex solvatation with neutral extractant molecules and the degree of complex polymerization.

The extraction constant K is then given as:

$$K = \frac{\left[(ML_n)_p . mHL\right]_o \left[H^+\right]_a^{np}}{\left[M^{n+}\right]_a^p \left[(HL)_2\right]_o^{(np+m)/2}} \tag{2-25}$$

The distribution coefficient $k_{M^{n+}}$ and percentage extraction can be derived in an analogous way as shown in Equations (2-14) and (2-15), respectively.

2.2.5.3. Mixed extractant systems

As mentioned in paragraph 2.2.4, improved extraction efficiencies can be obtained if mixtures of different extractants are applied in the extraction process, viz. the combination of a hydroxyoxime type reagent and an organophosphoric acid [2_11, 2_34-2_35]. The extraction reaction in the case of a mixed extractant system can be described in its simplest form as:

$$\left[M^{n+}\right]_a + n\left[HL\right]_o + y\left[HR\right]_o \leftrightarrow \left[ML_n . yHR\right]_o + n\left[H^+\right]_a \tag{2-26}$$

assuming only monomeric extractant molecules are involved in the extraction process. HL and HR denote the extractant which neutralizes the metal ion and the extractant which is responsible for the solvatation, respectively. n and y denote the amount of ligand molecules HL and HR which are respectively involved in the metal complex

The extraction constant can be written as:

$$K = \frac{\left[ML_n . yHR\right]_o \left[H^+\right]_a^n}{\left[M^{n+}\right]_a \left[HL\right]_o^n \left[HR\right]_o^y} \tag{2-27}$$

The distribution coefficient $k_{M^{n+}}$ and percentage extraction can be derived in an analogous way as shown in Equations (2-14) and (2-15), respectively.

Whether the hydroxyoxime or the organophosphoric acid is responsible for the neutralization of the complex is not clear [2_11, 2_35]. In a first study [2_35], it has been assumed that the hydroxyoxime is responsible for the solvatation of the nickel(II) complex extracted with 2-ethylhexanal oxime (EHO) and D2EHPA. A second study [2_11] investigated the mixed-ligand complexes of LIX 860-I and D2EHPA. In this study, it has been assumed that LIX 860-I, 5-dodecylsalicylaldoxime, is the chelating ligand, although it can also solvate the complex, whereas D2EHPA exclusively solvates the complex.

In Chapter 3, studies will be performed on the application of mixed-extractant systems for nickel(II), cobalt(II), copper(II), iron(II, III) and magnesium(II) extraction. FT-IR studies as well as UV-VIS absorption spectra will be made to gain further insight in the extraction mechanism.

2.3. SOLVENTS

Besides the choice of the carrier, the type of membrane solvent is also of primary importance in Supported Liquid Membrane processes. The choice of the organic solvent is extremely important in view of the stability of the liquid membrane. A detailed discussion of the stability and techniques for improving the stability will follow in paragraph 2.7. In fact, the membrane solvent must fulfil the following basic requirements [2_41]:

- low mutual solubility between organic and aqueous phase
- low volatility
- the organic liquid must be a solvent for the carrier and the carrier-solute complex
- surface tension must be lower than the critical surface tension of the support
- high solvent/water interfacial tension

Kerosene, a typical industrial solvent, is often used in liquid membrane processes [2_9]. Aliphatic hydrocarbons of higher boiling point are suitable membrane solvents. They have the additional advantage of being chemically more inert to polymeric solids [2_42]. Generally, aliphatic diluents are preferred to aromatic ones because of the lower losses [2_42]. The effectiveness of a solvent was studied in terms of the leakage of water across a polymeric membrane [2_42]. Figure 2-22 shows the rate-of-leakage curves for a polytetrafluoroethylene (PTFE) polymeric support. In Table 2-3, the physico-chemical properties at 25° C are mentioned of the organic solvents used.

Diluted sulphuric acid was circulated through the inside of the membrane fiber, while the outside stream consisted of deionised water. A pressure difference was set up between the two channel streams and a pH meter measured the change in hydrogen ion concentration in the water tank.

As Figure 2-22 shows, a fast leakage of water was detected for toluene, this in contrast to n-heptane and kerosene. The results above led to the conclusion that aliphatics are most suitable as membrane solvent, while aromatics show a trend of higher losses [2_42].

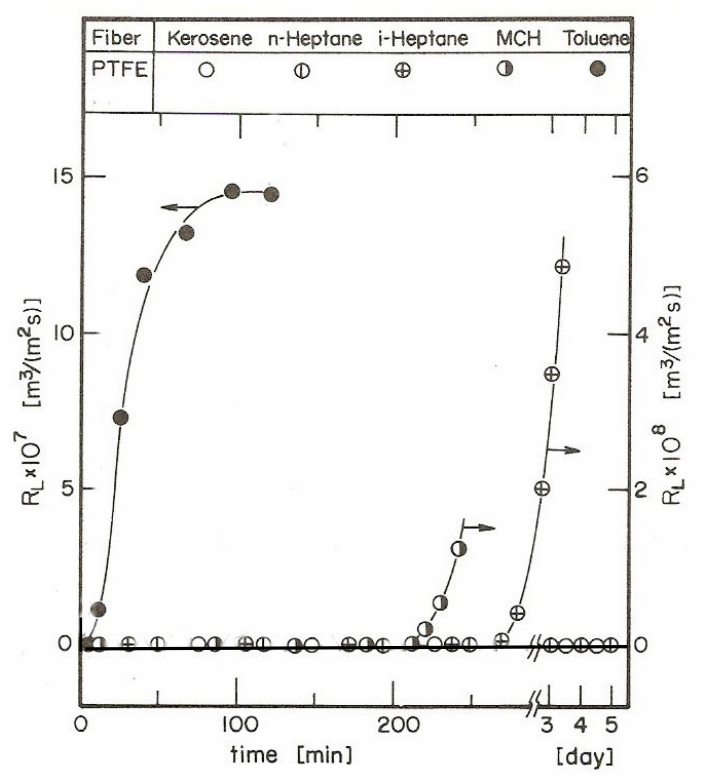


Figure 2-22. Influence of the type of solvent on the leakage rate of water across a PTFE membrane [2_42].

Table 2-3. Physico-chemical properties at 25° C of some organic solvents [2_42].

Organic Solvent	Surface tension σ x 10^3 (N.m^{-1})	Solvent-water interfacial tension γ x 10^3 (N.m^{-1})	Viscosity μ x 10^3 (Pa.s)	Density ρ x 10^{-3} (kg.m^{-3})
n-Heptane	19.6	50.8	0.382	0.684
iso-Heptane	-	32.7	0.43	0.705
Methylcyclohexane	23.3	41.1	0.659	0.771
Toluene	27.9	35.7	0.539	0.866
Kerosene	25.3	41.8	1.240	0.790

The choice of organic diluent is also closely related to the type of extractant, which has been chosen for a typical application. In certain cases, a specific amount of phase modifier is added to the organic phase in order to prevent third phase formation in contact with the aqueous phase. For instance, in the commercial use of organophosphorous extractant

systems, emulsion inhibitors such as tributyl phosphate and isodecanol are added [2_34]. In the commercial use of hydroxyoximes, such as LIX 860-I, 4-dodecylphenol is present in the extractant solution to improve its solubility characteristics [2_43]. Other long-chain alcohols which are frequently added as organic modifier are isotridecanol, 1-decanol and 4-nonylphenol [2_39].

When polar diluents such as alcohols are applied in the extraction process, the diluent is not only a carrier for the extractant and extracted metal complex, but also a participant in the extraction process. The effect of the diluent is essentially an organic phase reaction or interaction due to at least one of the following factors [2_39]. At first, interaction of the diluent with the extractant molecules affects the activity of the extractant and changes the extraction performance of the extractant. Secondly, interaction of the diluent with the extracted metal complex may change the composition of the complex through coordination and/or substitution of the diluent molecules. A typical example of the first category is the extraction of copper with a hydroxyoxime extractant. The hydroxyoxime has an oxime-hydroxyl group that behaves as an electron-acceptor. Therefore, the extraction of copper is lower by four to five orders of magnitude in electron-donor diluents (n-donor compounds such as alcohols and ketones) compared to non-polar hydrocarbons, without changing the composition of the extracted species due to the diluent-extractant interactions [2_39]. An example of the second category is the Cu(II)-D2EHPA complex. In literature [2_39], the absorption spectrum of the Cu(II)-D2EHPA complex was studied in various solvents. These absorption spectra are shown in Figure 2-23. In 2-ethyl hexanol, a solvent with electron donor ability, the absorption band of the complex is shifted to lower energies. The transformation of the approximately square planar configuration of the complex in inert solvents to a tetragonal one in the chemically active 2-ethyl hexanol is a plausible explanation [2_39]. This different behaviour implies that processes for solvent extraction must be developed for specially selected combinations of metal ion, extractant and diluent, sometimes making use of a modifier.

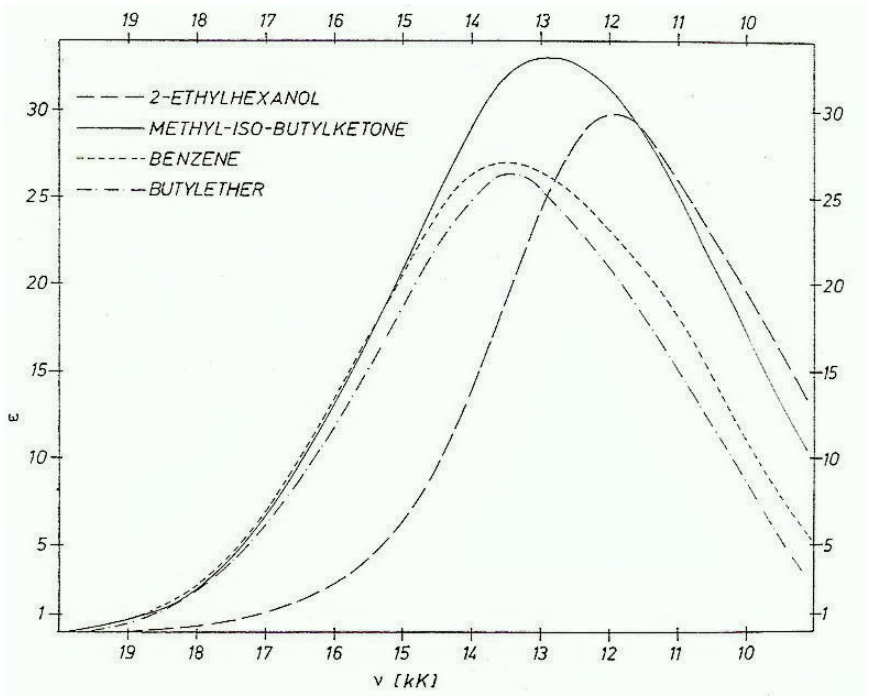


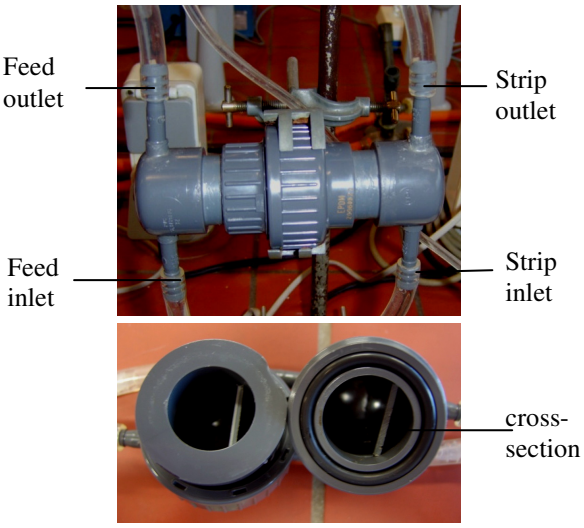
Figure 2-23. Absorption spectra (absorptivity versus frequency) of the Cu(II)-D2EHPA complex in various solvents [2_39]

(Conversion factor frequency: 1 kK ≅ 1344 cm^{-1})

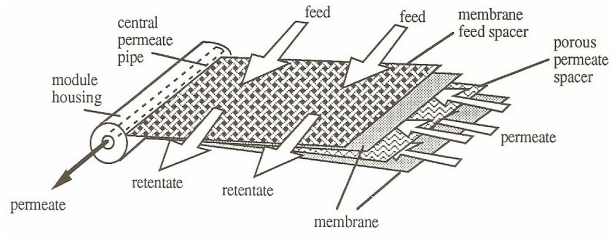
2.4. SUPPORT MEMBRANES

The third and last basic requirement for a Supported Liquid Membrane is the polymeric micro-porous support. Highly stable hydrophobic materials such as polypropylene (Celgard, Accurel) and polytetrafluoroethylene (Gore-Tex) are often used as supports. The function of the porous support membrane is to act as a framework for the extractant solution.

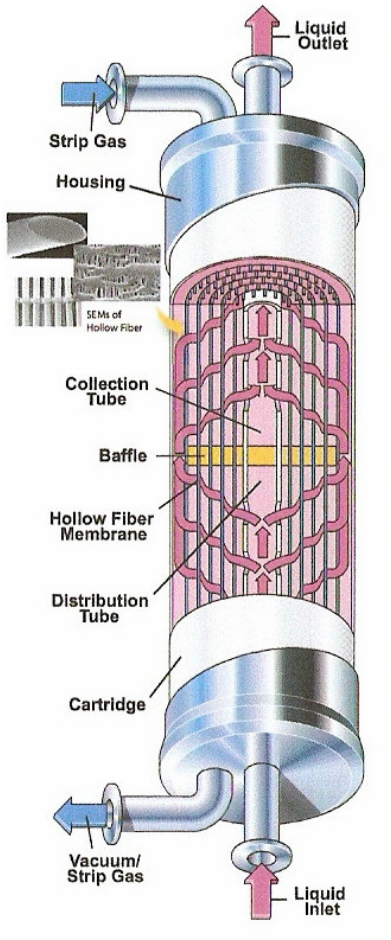
A planar or flat geometry is often used for small-scale laboratory purposes. Experimental designs usually consist of a two-compartment cell. For industrial purposes, the use of a planar geometry is not very effective since the ratio of surface area to volume is too low. Hollow fiber and spiral wound modules can be used to provide a high surface area to volume ratio [2_6]. The different configurations are depicted in Figure 2-24.



Two-compartment cell with flat membrane for lab-scale purposes



Spiral-wound module [2_5]



Hollow fiber Liqui-Cel Membrane contactor [2_44]

Figure 2-24. Different membrane configurations

The spiral-wound module is the next logical step from a flat membrane. It is in fact a plate-and-frame system wrapped around a central collection pipe, in a similar fashion to a sandwich roll [2_5]. The module with the highest packing density is however the hollow fiber module. The best known module designed for concentration-driven mass transfer is the Liqui-Cel® Extra-Flow module offered by Membrana (Celgard) which is also depicted in Figure 2-24. The patented Liqui-Cel Extra-Flow Membrane Contactor design contains thousands of micro-porous hollow fibers of polypropylene knitted into an array that is wound around a distribution tube with a central baffle. They offer membrane areas up to 130 m^2.

Initially, these modules were produced for removing CO_2, O_2 and N_2 from liquids or for adding CO_2, O_2 and N_2 to liquids in microelectronics, food and beverage, pharmaceutical,

industrial and analytic sectors [2_44]. During operation of the Liqui-Cel for gas-liquid applications, the liquid flows over the shell side (outside) of the hollow fibers. The Extra-Flow design incorporates a baffle in the middle of the contactor, which directs the liquid radially across the array. The baffle improves efficiency by minimizing shell side bypassing [2_44]. A strip gas or vacuum, either separately or in combination, is applied on the lumen side (inside) of the hollow fibers [2_44]. Because of its hydrophobic nature, the membrane acts as an inert support to allow intimate contact between the gas and liquid phase without dispersion [2_44].

The hollow fiber membrane contactor technology is also useful in liquid-liquid applications such as waste water treatment and metal ion extraction. The main challenge is to maximize the mass transfer rate by producing as much interfacial area as possible [2_44]. In liquid-liquid extraction, a high degree of extraction is often difficult to obtain when the solute containing feed is passed through the shell side, since this fluid is subject to bypassing and channeling. Therefore, in liquid-liquid extraction, the feed stream is usually sent through the fibers [2_44]. The characteristic properties of some hollow fiber polypropylene membranes of Celgard are shown in Table 2-4 and are compared with two flat membranes of Celgard.

Table 2-4. Characteristic properties of flat and hollow fiber polypropylene membranes of Celgard [2_44].

		Flat type membrane		Hollow fiber type	
Characteristic	Unit	Celgard 2400	Celgard 2500	X-40	X-50
Porosity	%	37	55	25	40
Pore size	µm	0.05	0.08	0.03	0.04
Thickness	µm	25	25	50	40
Fiber OD (nominal)	µm	-	-	300	300
Fiber ID (nominal)	µm	-	-	200	220

Liqui-Cel Membrane Contactors utilize the two primary fiber types X-40 and X-50. X-40 has a thicker wall with a smaller inside diameter, while the X-50 fiber has a slightly thinner wall with a larger inside diameter [2_44]. In fact, the surface porosity and overall porosity of the support materials should be high in order to obtain an optimal transport. On the other hand, the membrane thickness should be limited because the amount of species

transported across the membrane in function of time is inversely proportional to the membrane thickness [2_5].

2.5. THE ROLE OF AQUEOUS PHASE ADDITIVES

In order to enhance the efficiency of an extraction system, sometimes one or more extractants are combined in the organic phase, as already discussed in paragraph 2.2.4. Instead of using additives or mixtures of extractants in the organic phase, another method is described in literature to improve the liquid membrane extraction process. This method makes use of aqueous phase additives [2_46]. In fact, in the case of waste water treatment by means of liquid membranes, certain useful ligands may already be present in the waste water, thereby reducing the reagent cost. The extraction of heavy metals such as cobalt, copper and nickel can be improved by introducing anionic ligands to the aqueous metal solution [2_46]. The selected additive should be a weak complexing agent for the metal ions, rather than a strong one. Otherwise, it will prevent the extraction process. EDTA (ethylenediaminetetraacetic acid), for example, is such a strong complexing ligand with Co(II) that the extraction of the metal ion with D2EHPA is actually inhibited in the presence of EDTA in the aqueous phase. On the other hand, adding acetate to the aqueous solution accelerates the extraction of cobalt [2_46]. In literature [2_46], it was stated that the water molecules in the hexaaqueous cobalt(II) complex were replaced by the anionic ligand. Furthermore, the anionic ligand has a hydrophobic-hydrophilic nature. Therefore, it exhibits a surface-active property. The anionic ligand-metal complex tends to populate at the aqueous-organic interface more than the hydrated metal ions do. In this way, the metal ions are relatively concentrated at the feed/membrane interface. This is favourable for the membrane process and is called ligand-accelerated liquid membrane extraction.

The influence of the addition of several anionic ligands to the aqueous phase on the extraction of cobalt at an initial pH of 5.0 was studied in Emulsion Liquid Membranes containing D2EHPA as carrier molecule [2_46]. The results are shown in Figure 2-25.

Acetate (Ac^-) was found to produce the strongest effect on the extraction rate of cobalt. However, it must be noticed that the concentration of cobalt(II) never dropped to zero. On the contrary, the cobalt(II) concentration tends to increase slightly after 6 minutes in the case of acetate and succinate. In the case of cobalt extraction, an addition of 0.1 $mol.L^{-1}$ acetate showed the most profound effect. A further increase of the concentration had a negative influence on the extraction behaviour [2_46].

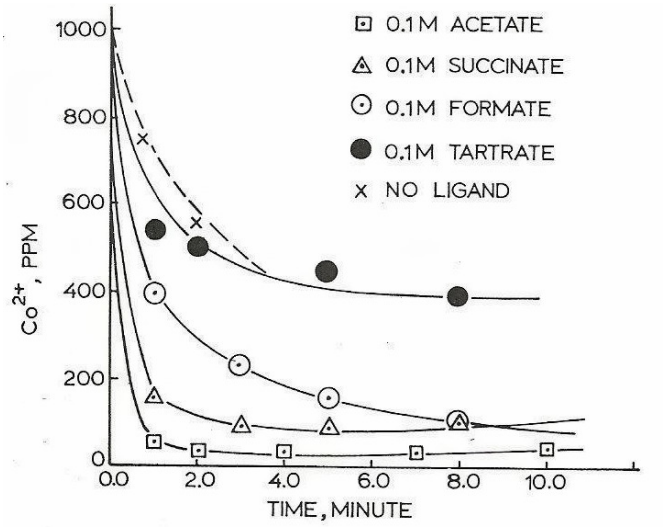


Figure 2-25. Influence of the additon of anionic ligands to the feed phase on the extraction of cobalt with D2EHPA [2_46].

The anionic ligands may act as a phase transfer catalyst. The introduction of auxiliary anionic ligands in the aqueous phase accelerates the extraction rate by forming an intermediate complex in which at least one coordinated water molecule surrounding the metal ion has been replaced. In practice, the ligand effect in the liquid membrane extraction could result in a shorter contact time between the two phases. NMR spectra of the cobalt(II) complexes with and without acetate in the aqueous phase showed that the acetate ions did not enter into the organic phase to form a Co-D2EHPA-HAc complex [2_46]. Similar effects have been found for the liquid membrane extraction of nickel(II) and copper(II) by D2EHPA [2_46].

Acetate ions can also be used as a buffering agent for model or reference solutions [2_47-2_48]. As a result of the protonation of the acetate, free acetic acid is formed, which can be distributed between both aqueous and organic phase. The metal extraction can also be influenced by the absorption of acetate anions or acetic acid at the interface. In this way, acetate ions act as an extraction catalyst [2_46].

Sodium acetate was used in model solutions to study the effects of salts on the kinetics of the extraction of cobalt(II) and zinc(II) by D2EHPA dissolved in n-dodecane [2_48]. Faster kinetics were found in the presence of acetate ions for the extraction of the cobalt(II)

ion. Prior complexation of metal ions by acetate was observed to promote the subsequent reaction with the extractant [2_48]. Another study [2_49] tried to gain a better insight in the composition of the cobalt complexes extracted in the presence of acetate ions. CYANEX reagents were used as extractants diluted in toluene. An extractant:metal ratio of 2:1 was revealed for CYANEX 272 and 302 with cobalt(II), while, for CYANEX 301 an extractant:metal ratio of 1:1 was observed [2_49]. The plot of log k versus log [acetate] showed however that acetate ions were present in the organic extract [2_49]. These findings received additional support from their Infrared spectral studies, but are in contradiction to the results of the NMR spectra of the cobalt-D2EHPA complexes mentioned before [2_46].

The research concerning aqueous phase additives was mainly focussed on the extraction of cobalt ions with D2EHPA and CYANEX 272, 302 and 301 [2_46-2_49]. Nevertheless, it is also worth evaluating the influence of aqueous phase additives on other extraction mechanisms. Acetate ions can be used as a buffering agent and prior complexation of metal ions by acetate seems to promote the subsequent reaction with the extractant. If acetate/acetic acid also enters into the organic phase is not clear yet. Therefore, the influence of the addition of acetate ions on the extraction of cobalt(II), nickel(II), copper(II), iron(II, III) and magnesium(II) will be investigated in Chapter 3. As extractants, D2EHPA, CYANEX 301 and LIX 860-I will be applied. The extractants will be investigated separately as well as in mixtures of extractants. Furthermore, Infrared spectral studies as well as UV-VIS absorption spectra will be made to distinguish if acetate/acetic acid also participates in the formation of the metal-organic complexes.

2.6. KINETICS OF THE EXTRACTION PROCESS AND RELATED DEFINITIONS [2_5]

Most of the research is concentrated on the study of two main parameters with the aim of improving the performance of SLM: flux or permeability and stability. Within this paragraph, the flux and permeability will be defined. The discussion of the stability will follow in paragraph 2.7.

The kinetics of the transport of a metal ion through a liquid membrane with an acidic carrier will be reduced to the discussion of the simplified case of monomeric extractant molecules involving no complex solvatation and polymerization (see Figure 2-26).

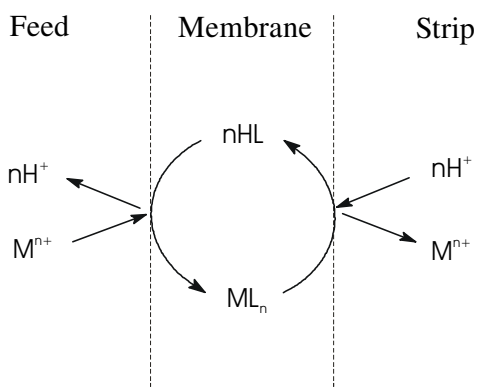


Figure 2-26. Schematic representation of metal ion transport through a Supported Liquid Membrane containing an acidic extractant molecule

In the case of an acidic carrier, the transport of a metal ion M^{n+} is enhanced by the presence of protons in the strip solution [2_5]. The metal ion M^{n+} and carrier HL form the complex ML_n, which diffuses through the membrane.

The following steps can be distinguished during the transport mechanism:

1) Diffusion of the metal ions M^{n+} from the bulk feed phase to the feed/membrane interface.
2) At the feed/membrane interface, the complexation reaction takes place between n carrier molecules HL and the metal ion M^{n+}. At the same time, n H^+ are released in the feed phase and diffuse into the direction of the bulk feed phase.
3) The carrier-metal complex diffuses through the organic membrane into the direction of the membrane/strip interface.
4) Protons diffuse from the bulk strip phase into the direction of the membrane/strip interface. At the membrane/strip interface, the decomplexation reaction or back-extraction reaction takes place. The metal ion M^{n+} is released into the strip phase and free carrier is formed.
5) The free carrier HL diffuses back to the feed/membrane interface where it can form a complex with a new metal ion.
6) The metal ion diffuses towards the bulk strip phase.

As can be seen from Figure 2-26, the transport of the metal ion depends on the rate of complex formation (complexation/decomplexation) at the two interfaces, but also on the diffusion of free carrier and metal complex across the membrane [2_5].

Three processes must be considered in the description of the overall transport of a metal ion through a hollow fiber [2_5]. The flow of metal ions in the boundary layer (J_{bl}) is given by:

$$J_{bl} = -D_{bl} \frac{d\left[M^{n+}\right]_a}{dx} \tag{2-28}$$

with D_{bl} the diffusion coefficient of the metal ions through the boundary layer.
Integration of Equation (2-28) over the boundary layer under steady-state conditions gives:

$$\overset{0}{n}_{M^{n+},bl} = \Omega_{\text{int}} \frac{D_{bl}}{\delta_{bl}} \left(\left[M^{n+}\right]_a - \left[M^{n+}\right]_{a,i} \right) \tag{2-29}$$

where $\overset{0}{n}_{M^{n+},bl}$ is the molar flux of metal ions through the boundary layer, Ω_{int} is the interfacial surface area and δ_{bl} is the thickness of the boundary layer. The subscript i indicates that the concentration is an interfacial concentration. At the interface, the complexation reaction takes place. Assuming that this reaction is intrinsically very fast, then the concentrations at the interface will be almost equal to the equilibrium concentrations. This means that:

$$k_{M^{n+}} \approx \frac{\left[ML_n\right]_{o,i}}{\left[M^{n+}\right]_{a,i}} \tag{2-30}$$

The flux of metal ions through the membrane phase (J_m) is given by:

$$J_m = -D_m \frac{d\left[ML_n\right]_o}{dx} \tag{2-31}$$

Assuming that the concentration $\left[ML_n\right]$ at the interface between membrane and strip phase is zero as a result of the very acidic strip solution and the kinetics of the stripping reaction is intrinsically very fast, integration of Equation (2-31) over the membrane results in:

$$\overset{0}{n}_{M^{n+},m} = \Omega_{\ln gem} \frac{D_m}{l} \left(\left[ML_n\right]_{o,i} - 0 \right) \tag{2-32}$$

where $\overset{0}{n}_{M^{n+},m}$ is the molar flux of metal ions through the membrane phase, l is the membrane thickness and $\Omega_{\ln gem}$ the logarithmic mean value of the surface area.

Under steady-state conditions the molar flow of metal ions through the boundary layer and through the membrane phase are equal (otherwise accumulation would occur in the organic phase), i.e. $\overset{0}{n}_{M^{n+},bl} = \overset{0}{n}_{M^{n+},m}$ and, in addition, are equal to the overall molar flow $\overset{0}{n}_{M^{n+}}$. Assuming $\overset{0}{n}_{M^{n+}} = JA$ with $A=\Omega_{int}$ and combining Equations (2-29), (2-30) and (2-32) gives:

$$J = \frac{k_{M^{n+}}\left[M^{n+}\right]_a}{k_{M^{n+}}\frac{\delta_{bl}}{D_{bl}} + \frac{l}{D_m}\frac{A}{\Omega_{\ln gem}}} = P\left[M^{n+}\right]_a \qquad (2\text{-}33)$$

and is valid for low metal concentrations.

In the case of a recirculation experiment, the metal ion concentration in the feed, $[M^{n+}]_a$, is not constant but decreases as a function of time. The flux ($g.m^{-2}.h^{-1}$) is then given by:

$$J = -\frac{V}{A}\frac{d\left[M^{n+}\right]_a}{dt} \qquad (2\text{-}34)$$

where V is the total feed volume (m^3), A is the membrane area (m^2), $\left[M^{n+}\right]_a$ is the metal concentration ($g.m^{-3}$) and t is the time expressed in hours (h).

The permeability P is a measure for the ease of transport of a solute through a specific area of membrane surface in a given unit of time and can be calculated with the following Equation:

$$P = \frac{J}{\left[M^{n+}\right]_a} \qquad (2\text{-}35)$$

where P is the permeability coefficient ($m.h^{-1}$).

2.7. STABILITY RELATED TO TECHNOLOGICAL CONFIGURATIONS AND INNOVATIONS

Supported Liquid Membranes are an attractive alternative to conventional liquid-liquid extraction processes and other separation techniques (see also Chapter 1). Despite all of its advantages, Supported Liquid Membranes are not used at a large scale in the industry nowadays. The major reason for this is the membrane stability or lifetime, which makes that the industry is rather reserved to implement the Supported Liquid Membrane technology, although lifetimes of 1500 hours have been achieved without further measures [2_50]. When

this instability phenomenon occurs varies a lot and depends mainly on the extraction system of the process [2_51]. Nevertheless, given the essential need for metal ion recovery as well as for the extraction of numerous small organic compounds over the last two decades in hydrometallurgy, biotechnology and in the treatment of industrial waste water, significant scientific effort has been made to understand and improve the stability of liquid membranes.

Instability of SLM is mainly due to the loss of carrier and/or organic solvent out of the pores of the supporting layer [2_42, 2_51]. The lifetime of the membrane is greatly influenced by the solubility of the carrier and/or membrane solvent in both the feed and strip phase [2_51]. In the case of D2EHPA, for instance, the solubility in water increases with an increasing pH [2_51]. In fact, the carrier hydrophobicity and its surface activity, together with its solubility in the membrane solvent, are important for the stability. The more surface active the carrier is the less stable is the membrane [2_51]. However, even if the solubility of the organic phase in the aqueous phase is very low, the process becomes unstable after a finite period of time since the membrane solvent is held in the pore structure solely by capillary forces [2_42, 2_51].

When the pressure difference across the membrane exceeds a critical value, the liquid membrane phase is pushed out of the pores of the support. The critical displacement pressure P_c for an SLM can be defined as the minimum transmembrane pressure required to displace the impregnating phase out of the largest pore. For a cylindrical capillary, the critical displacement pressure can be quantified by the Equation of Young and Laplace:

$$P_c = \frac{2\gamma \cos\theta}{r} \tag{2-36}$$

where P_c is the critical displacement pressure ($N.m^{-2}$), γ is the interfacial tension between strip or feed solution and the liquid membrane phase ($N.m^{-1}$), θ is the contact angle between the membrane pore wall and the impregnating liquid and r is the pore radius (m). The critical displacement pressure P_c can be calculated by stating cos θ equals to unity ($\theta = 0°$) [2_51]. Equation (2-36) can be applied on porous membranes, assuming that the pores can be considered as a bundle of uniform cylindrical capillaries. However, commercial supporting membranes do not have uniform cylindrical capillaries and the distribution of pore sizes is large, which makes that Equation (2-36) is only a general prediction [2_51]. In fact, as long as the transmembrane pressure is smaller than the critical pressure, the liquid membrane phase will not be replaced by the aqueous feed or strip solutions. To obtain a stable liquid membrane, the transmembrane pressure differences should be minimized [2_51]. Otherwise,

the flux will decrease due to the loss of carrier and solvent. In Chapter 5, the breakthrough pressures of different flat membranes will be determined.

Also fouling and subsequent blocking of the support pores can cause a flux decay with time [2_42, 2_51].

In fact, a careful choice of membrane and operating conditions and materials is important to maximize the membrane lifetime. In paragraphs 2.3 and 2.4, some guidelines have already been given concerning the ideal type of solvent and support material. Several physical and physicochemical properties have been correlated with SLM stability: pore diameter, support thickness, dielectric constant of the solvent, viscosity, interfacial tension, contact angle, bubble and drop points, water solubility and osmotic pressure gradient [2_51]. Aliphatic hydrocarbons of high boiling point are most suitable as membrane solvent, while aromatics show a trend of higher losses [2_42]. Furthermore, they have the additional advantage of being chemically more inert to polymeric solids [2_42]. Systems which are characterized by high organic/water interfacial tensions and a low solubility of water in the organic phase should be used [2_42, 2_50]. Emulsification of the organic phase due to lateral shear forces must be avoided [2_50]. In addition, the organic membrane phase should have a surface tension, which is smaller than the critical surface tension of the support [2_42, 2_51]. Supports with a small pore size should be used - see Laplace Equation (2-36) -, although the surface porosity should be high enough to obtain a reasonable flux [2_51]. The flux is also partially determined by the membrane thickness. The higher the membrane thickness, the more stable the liquid membrane because the support contains more extractant phase. On the other hand, an increase of the thickness may also limit the fluxes of the solutes across the membrane. Limited fluxes are also encountered if the organic phase exhibits a too high viscosity [2_51]. The viscosity decreases with increasing temperature. But, in general, membrane lifetime is usually lower when temperature increases [2_51].

Several suggestions for lifetime improvement can be found in literature and are situated at a more technological level [2_4, 2_51]. The Supported Liquid Membrane technology consists of impregnating the micro-porous walls of the polymeric support with the carrier solution. Usually, the feed solution is circulated through the lumen side and the strip solution on the shell side of the hollow fiber. In such a case, extraction and back extraction of the metal species take place simultaneously. This technology or operation mode has been the subject of extensive studies during the past years at vzw KaHo Sint-Lieven R&D [2_52]. One of the possibilities to enhance the lifetime is reimpregnation of the support with the liquid membrane phase. Different methods are described in literature [2_51]. Reimpregnation is

possible by forcing the original extractant solution to flow at the lumen side of the membrane instead of the aqueous feed solution for a few minutes or by an injection mechanism [2_51]. An alternative method is adding a small amount of organic phase to the strip solution. The organic phase can refill the vacant pores continuously with fresh liquid membrane phase [2_51]. A major disadvantage of this method is that feed and/or strip solutions are polluted with the membrane liquid in the same order of magnitude as in ordinary solvent-solvent extraction [2_51]. By reimpregnation, the effects of liquid membrane loss are cured, but the problem of instability itself is not tackled. Gelation of the liquid membrane phase seems very encouraging [2_51]. The resistance against liquid displacement out of the support pores will be enhanced and emulsification will be prevented [2_51]. This gelation can be done by creating a homogenous gel network in the support pores or by applying a thin layer (< 2 µm) on the feed side of the support, although its industrial applicability is questioned [2_51].

In addition, new liquid membrane configurations are extensively studied. These configurations combine the concept of Supported Liquid Membranes and Bulk Liquid Membranes [2_42, 2_51]. In a first mode, the support is not impregnated with the extractant solution, but the feed is sent through the lumen side, while the organic phase is pumped through the shell side of the hollow fiber module. The aqueous and organic solution come into contact through the pores of the fiber wall [2_51]. However, within this mode, only one separation operation is realized in one liquid membrane contactor, viz. extraction or back-extraction. Also other variations on the previous mode exist, e.g. the Flowing Liquid Membrane (FLM) configuration and Contained Liquid Membranes (CLM) [2_51]. In FLM, the liquid membrane phase flows in thin channels between two hydrophobic microfiltration membranes [2_51]. These micro-filtration membranes separate the organic phase from feed and strip, and form in this way a stable liquid membrane. A schematic representation of the Flowing Liquid Membrane configuration is given in Figure 2-27 [2_51].

In Figure 2-27, an example of a schematic drawing of a Contained Liquid Membrane is also shown (CLM). The idea of Contained Liquid Membranes was first developed in the late eighties by the Sirkar group [2_51]. In a CLM, two sets of hollow fibers are present (see Figure 2-27). One set of hollow fibers is used for the feed solution, the other set is used for the strip solution. Both aqueous phases flow through the lumen side of the fibers [2_51]. The hollow fibers are well mixed throughout the contactor, but they are separated at the end. The fibers can be either hydrophilic or hydrophobic.

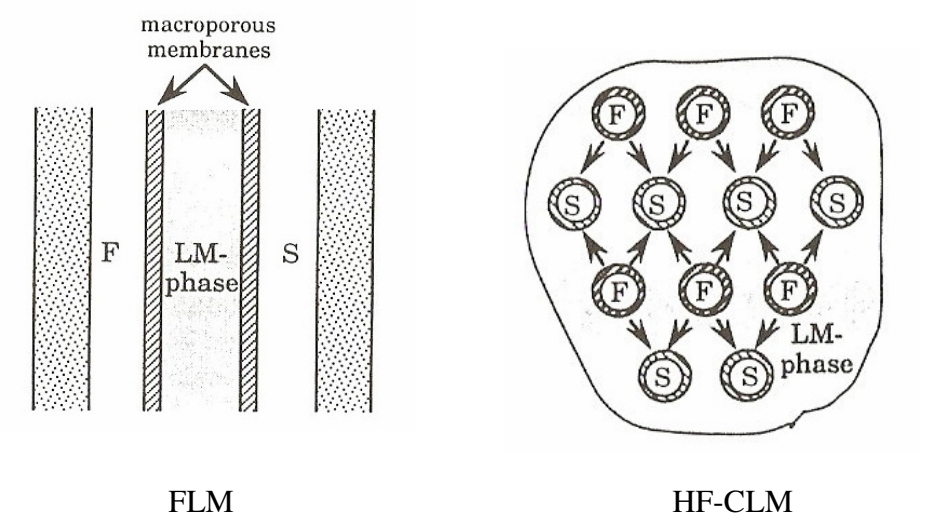


Figure 2-27. Schematic drawing of Flowing Liquid Membrane (FLM) and Hollow Fiber Contained Liquid Membrane (HF-CLM) [2_50]

If the fibers are hydrophilic, the aqueous phases fill the pores of the fiber. On the other hand, the fibers are wetted by the organic membrane phase when the fibers are hydrophobic [2_51]. The membrane phase contains a complexing agent which binds at the interface in one set of the fibers with one of the components of the feed solution [2_51]. The complex diffuses across the liquid membrane and dissociates in the other set of fibers where the component is released into the strip solution [2_51]. Stabilities up to 60 days were reported [2_51]. Loss of liquid membrane phase is also a problem for these operation modes, which combine the concept of SLM and BLM. Moreover, the processes are more complicated than in SLM, while the total resistance to permeation of solute from feed to strip increased [2_51]. Finally, these membrane configurations generally need a much larger amount of liquid membrane phase than Supported Liquid Membranes, which might be disadvantageous when expensive extractants are used [2_51].

The stability of a Supported Liquid Membrane can also be improved by attaching the carriers or extractants covalently onto the polymer. This technique is also called Immobilized Liquid Membranes (ILM) or fixed-site carrier membranes [2_53, 2_54]. Applications for new reactive polymers containing functional groups are continually growing. Functional polymers represent an important class of polymeric materials, which contain the functional groups in the main or side chains [2_54]. Their synthesis is performed by means of classical

methods such as: polymerisation or polycondensation of functional monomers, as well as by the chemical modification of some polymers [2_54]. However, in many circumstances, the chemical modification is the most frequently used method [2_54]. Most of the research on functional polymers has been focussed on the modification of resins (ion exchange resins) instead of polymer films [2_54]. The transport mechanism of a solute through the chelating membrane is different compared to SLM. In a pioneering work [2_15], the "chained carrier" theory or "fixed-site jumping mechanism" was proposed to describe the facilitated transport process in a solid membrane where mobility of the carrier is restricted. More important is that they demonstrated that membranes with immobilized carriers may show a percolation threshold, i.e. the carrier concentration must be sufficiently high so that a continuous chain across the membranes can be formed, although fluxes are still rather limited in solid membranes compared to liquid membranes [2_15].

Finally, during the last years, a lot of attention has been paid on a novel type of liquid membrane, called Polymer Inclusion Membranes (PIM), although a number of other names are also being used such as polymer liquid, gelled liquid, polymer plasticized, solvent polymeric or fixed-site carrier membranes. This last name is also used in the context of ILM, which may cause some confusion [2_15]. PIM membranes are formed by casting a solution containing an extractant, a plasticizer and a base polymer such as cellulose triacetate (CTA) or polyvinylchloride (PVC) to form a thin, flexible and stable film [2_15]. The resulting self-supporting membrane can be used to separate selectively the solutes of interest in a similar way as in SLM [2_15]. In several studies, PVC has been used to gel the liquid phase of an SLM to stabilize it within the pores of an inert support, as discussed before. In these cases, the PVC concentration of the membrane is much lower than that used for a self-supporting membrane. PIM membranes retain most of the advantages of SLM while exhibiting a good stability and versatility [2_15]. It is also claimed that the lower diffusion coefficient often encountered in PIM membranes can be easily offset by creating a thinner membrane in comparison to its traditional SLM counterpart [2_15], although this seems very doubtful in order to maintain its mechanical properties. It is also interesting to note that PIM membranes have been used in chemical sensing for more than 30 years in the form of polymer membrane ion-selective electrodes (ISEs) [2_15]. However, the requirements for the membrane characteristics are somewhat different for the two applications [2_15]. In sensing, fast ion exchange or metal ion complexation is required at the sample solution/membrane interface to rapidly establish the electrical potential difference but there should be negligible transport of the metal containing species through the membrane within the timeframe of the

measurement [2_15]. In separation, fast interfacial reactions are required, but in this case, high diffusion coefficients of the metal containing species within the membrane are also desirable in order to achieve mass transport from the source to the receiving phase within a reasonable timescale [2_15]. Both SLM and PIM involve the selective transport of a target solute from one aqueous solution to another by means of the membrane. The overall transport consists of two main processes, namely the transfer of the target solute across the two interfaces and diffusion through the membrane [2_15]. The former process is similar for both types of membranes, however, because PIM membranes are distinctively different from SLM in their composition and morphology, the actual bulk diffusion mechanisms within the membrane phase can be quite different [2_15]. In fact, because the carrier is not covalently bound to the base polymer, it may be assumed that the actual diffusion mechanism is intermediate between mobile carrier diffusion and fixed-site jumping [2_15].

Summarized, it has to be mentioned that a comparison between all these types of configurations and stabilizing methods discussed above is required in order to decide which system is the best option for application in a particular process. Besides the system's performance, economical factors play also an important role in determining the final choice.

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Chapter 3

FUNDAMENTAL STUDY OF THE INFLUENCE OF MIXED EXTRACTANT SYSTEMS AND AQUEOUS PHASE ADDITIVES ON THE EXTRACTION BEHAVIOUR OF COBALT(II), COPPER(II), NICKEL(II), IRON(II,III) AND MAGNESIUM(II) IN DIFFERENT TYPES OF SOLVENTS

A thorough study of the different process parameters in liquid membranes is of major importance for determining an optimal extraction system for a specific metal ion under well-defined practical circumstances. One of these process parameters is the carrier system, which plays a crucial role in the extraction process, as already mentioned in paragraph 2.2. Therefore, a careful choice of the carrier or extractant is a necessary prerequisite. In the case of the metal ions cobalt(II), copper(II), nickel(II) and iron(III), acidic extractants are frequently used for solvent extractions [3_1-3_5]. LIX 860-I or 5-dodecylsalicylaldoxime is for instance a very efficient extraction agent for copper(II) [3_1]. For other metal ions, viz. nickel(II) and cobalt(II), the kinetics of the extraction process are rather limited when an acidic extractant is used in the extraction process [3_2-3_3].

During the past, a lot of research has been focussed on improving extraction processes, especially those for cobalt(II) and nickel(II). Two methods are described in literature. The first method makes use of a combination of two or more extractants in the organic phase [3_3-3_7] (see paragraph 2.2.4), whereas the second method is focussed on aqueous phase additives [3_8-3_11] (see also paragraph 2.5). In the case of waste water treatment by means of liquid membranes, certain useful ligands may already be available in the effluent streams resulting in an improvement of the separation process.

By combining two or more types of extractants, synergistic effects may occur [3_3-3_7]. In this way, a mixture of two or more extractants produces an extraction percentage which is higher than the sum of the extraction percentages obtained with each extractant independently. One extractant complexes the metal ion and neutralizes the charge

while another extractant may replace water molecules or may occupy free coordination sites [3_3-3_7]. However, the addition of a second carrier may also have a deleterious influence on the extraction equilibrium when the second carrier can interact with the first extractant through the formation of hydrogen bonds. Such interactions therefore compete with the metal extraction reaction. Furthermore, a decrease of the selectivity can occur. A decrease of the selectivity of Co/Ni separation was for instance ascertained during the extraction of cobalt(II) with the organophosphinic extractant CYANEX 272 when a modifier was added to the organic phase such as TBP, TOPO, p-nonylphenol or isodecanol [3_12].

Among the different extractant combinations, mixtures of acidic carriers and oximes have been used extensively, whereas combinations of two acidic extractants are less common [3_3-3_7]. Improved extraction of divalent transition metal ions has been found with mixtures of an oxime of aliphatic aldehydes and an organophosphoric acid [3_3], the enhancements of extraction increasing in the order Fe(II) < Co(II) < Cu(II) < Ni(II). The highest improvement was found for nickel extraction and the selectivity of cobalt over nickel shown by a single organophosphoric acid such as D2EHPA was reversed [3_4-3_5] (see also paragraph 2.2.4). Synergism has also been observed when pyridinecarboxylate esters or alkylpyridines and carboxylic acids were combined [3_6-3_7]. By adding pyridinecarboxylate esters to carboxylic acids, substantial shifts were found in the pH_{50} values for the extraction of Ni(II) and Co(II). In fact, synergism has been shown to occur in many mixed solvent systems, but the actual mechanisms involved are still largely unresolved.

The second method makes use of the addition of certain anionic ligands, viz. acetate ions, to the aqueous metal solution [3_8-3_11]. Whether these anions really participate in the formation of the organic metal complex is not always unequivocal as already discussed in paragraph 2.5.

A lot of the research has been focussed on the extraction of cobalt(II) [3_8-3_11]. On the one hand, water molecules in the hexaaqueous cobalt(II) complex can be replaced by the anionic ligand [3_8]. This ligand-cobalt(II) complex reacts quickly with the extractant and therefore enhances the reaction rate. Furthermore, the anionic ligand has a hydrophobic-hydrophilic molecular structure; therefore it exhibits a surface-active property. The anionic ligand-metal complex tends to gather at the aqueous-organic interface more than the hydrated metal ions do [3_8]. In this way, the metal ions are relatively concentrated at the membrane interface. This is favourable to the kinetics of the membrane extraction process and is called ligand-accelerated liquid membrane extraction [3_8]. On the other hand,

acetate/acetic acid can also be used as buffering agent for model or reference solutions [3_9-3_10]. As a result of the protonation of acetate, free acetic acid is formed, which can be distributed between both aqueous and organic phase.

In this Chapter, the influence of mixed extractant systems as well as the influence of acetate ions on the extraction behaviour of Cu(II), Ni(II), Mg(II), Co(II) and Fe(II, III) is studied. Infrared and UV-VIS absorption spectra of the metal-organic complexes will be used to gain insight in the complexation characteristics and to identify if acetate/acetic acid enters into the organic phase. These studies are mainly focussed on D2EHPA, CYANEX 301 and LIX 860-I. The extraction reagents are investigated separately as well as in their respective mixtures to remark synergistic effects. Furthermore, two different diluents are chosen for this study: namely hexane and 1-decanol. In fact, kerosene is often used in liquid membrane processes (see paragraph 2.3). Kerosene of technical grade is however not suitable for the spectrophotometric analysis. Therefore, hexane (previously distilled) is applied as organic diluent instead of kerosene and a comparison is made with a more polar diluent, viz. the higher alcohol 1-decanol. Hexane is expected to provide similar extraction behaviour as kerosene, but must be avoided in industrial applications due to safety reasons. When polar diluents, such as alcohols, are applied in the extraction process, the diluent is not only a carrier for the extractant and extracted metal complex, but may also participate in the extraction process (see also paragraph 2.3). Possible changes in spectral data are investigated, besides the effect that polar diluents may have on the extraction efficiency of the metal ions.

3.1. GENERAL PROCEDURE

Liquid-liquid extractions were performed to study the influence of mixed extractant systems, diluent type and the addition of aqueous phase additives on the extraction efficiency of Co(II), Ni(II), Cu(II), Fe(II, III) and Mg(II). Infrared and UV-VIS absorption spectra were taken of the various organic phases to investigate any changes in complex formation.

Stock solutions of metal ions were prepared using the appropriate amount of the chloride salt. Hexane and 1-decanol were used as organic diluents for the extractants D2EHPA, LIX 860-I, CYANEX 301 and their mixtures. The physical properties of the extractants are included in Annex A [3_1, 3_12-3_13]. As can be seen in Table A-3, LIX 860-I contains only approximately 20% 5-dodecylsalicylaldoxime. Therefore, all fundamental studies were performed with 5-dodecylsalicylaldoxime, which was kindly supplied by Cognis Inc.

In a separation funnel, 10.00 mL metal solution - 0.0500 mol.L^{-1} - was added to 10.00 mL of organic solution containing 0.250 mol.L^{-1} extractant diluted with hexane or 1-decanol giving a ratio of mol HL/mol M^{n+}= 5/1 where M^{n+} and HL stand for metal ion and extractant respectively. In the combined organic solutions, each extractant was present in a concentration of 0.250 mol.L^{-1}. Co(II), Ni(II) and Mg(II) solutions had an initial pH of 5.0. Cu(II) solutions were used with an initial pH of 3.0, Fe(III) solutions had a pH of 1.5 and Fe(II) solutions were made with $(NH_4)_2Fe(SO_4)_2$ at an initial pH of 1.0. pH adjustments were made with hydrochloric acid or sodium hydroxide.

At room temperature, the funnel was placed into a shaker for a whole night. After separation of the two phases, the equilibrium pH was measured as well as the metal concentration in the aqueous phase, after appropriate dilution. From the organic phase, an FT-IR spectrum was taken in the range 4000-500 cm^{-1} and the UV-VIS spectrum was recorded from 190 to 900 nm, if necessary, after appropriate dilution.

The first set of experiments was repeated with an aqueous phase containing additionally 0.25 mol.L^{-1} acetate ions prepared from the corresponding sodium salt. The same procedure was used as described above.

3.2. INFLUENCE OF SOLVENT, MIXTURES OF EXTRACTANTS AND ACETATE IONS ON THE EXTRACTION BEHAVIOUR OF COPPER(II), NICKEL(II), COBALT(II), IRON(II, III) AND MAGNESIUM(II)

In the succeeding paragraphs, the extraction results will be presented and discussed for each metal ion separately. The extraction results are expressed as extraction percentages instead of the distribution coefficient k (see paragraph 2.2.5.1). Hence, a question of accuracy disappears in the case of very high values of k when extraction percentages are used. FT-IR and UV-VIS absorption spectra of the metal complexes will be discussed in paragraphs 3.3 and 3.4, respectively.

3.2.1. Copper(II)

3.2.1.1. Influence of the type of solvent (in the absence of acetate ions)

The extraction results of copper(II) with D2EHPA, LIX 860-I and CYANEX 301 in hexane and 1-decanol are shown in Figure 3-1. The extraction data and corresponding equilibrium pH values are shown in Annex B (Table B-1).

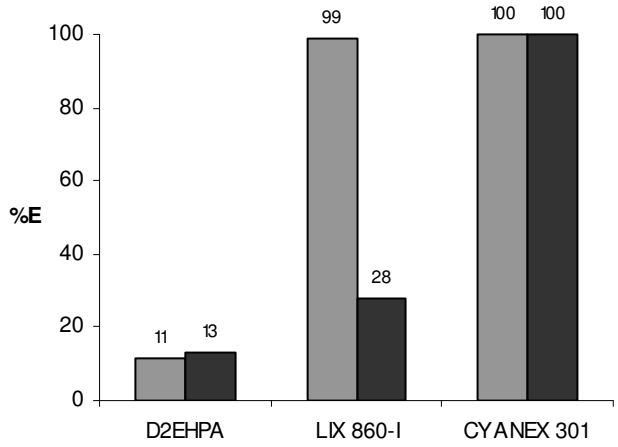


Figure 3-1. Extraction of Cu(II) with different extractants diluted in hexane (■) and 1-decanol (■)

Hexane

As can be seen in Figure 3-1, Cu(II) is extracted efficiently in hexane with LIX 860-I and with CYANEX 301. With D2EHPA, only 11% of copper(II) is extracted. LIX 860-I is a well-known extraction agent for copper(II). This can be documented by several studies on the removal of Cu(II) from simulated and industrial waste water with the Supported Liquid Membrane technology [3_14-3_15]. CYANEX 301 has the ability to extract several metal ions at low pH [3_13]. An important drawback of CYANEX 301 is however the formation of very strong complexes with copper(II), resulting in a very difficult decomplexation [3_16].

1-Decanol

The extraction efficiency of Cu(II) with D2EHPA did not change when 1-decanol was used as diluent, this in contrast with the extraction performance of LIX 860-I. A big decline in extraction percentage was found in the presence of the higher alcohol 1-decanol. With CYANEX 301, 100% extraction was obtained in both diluents.

The effect of the diluent can be explained by means of an organic-phase reaction or interaction (see also paragraph 2.3) [3_17].

The lower amount of copper(II) extracted in 1-decanol with LIX 860-I can be explained by the fact that the active component of LIX 860-I, a hydroxyoxime, contains an oxime-hydroxyl group (see Figure 3-2) that behaves as an electron-acceptor [3_17]. Therefore the hydroxyoxime reagent can react with a diluent with electron-donor properties, such as ethanol or 1-decanol, resulting in a lower extraction efficiency of LIX 860-I for copper(II) in electron-donor diluents than in non-polar hydrocarbons.

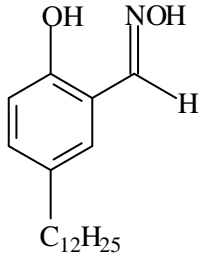


Figure 3-2. Structure of LIX 860-I

The P→O group of acidic organo-phosphorous compounds, e.g. D2EHPA (see Figure 3-3), belongs on the other hand to the n-donor solvent class. The interaction between extractant and diluent can therefore be expected to be moderate [3_17].

With CYANEX 301, the dithiosubstituted organophosphinic acid, good extractions were obtained in hexane and 1-decanol.

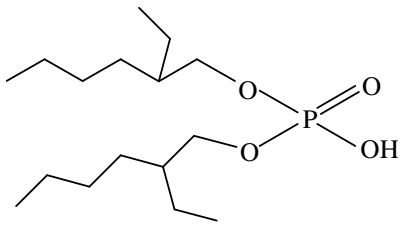


Figure 3-3. Structure of D2EHPA

3.2.1.2. Synergism (in the absence of acetate ions)

By combining two or more types of extractants, synergistic effects may occur. Therefore, the extraction efficiency of the respective mixtures of the extractants were also

investigated for copper(II) extraction and compared to the separate use of the extraction reagents. The extraction results of copper(II) in hexane and 1-decanol are shown in Figure 3-4. The extraction data and corresponding equilibrium pH values are included in Annex B (Table B-1).

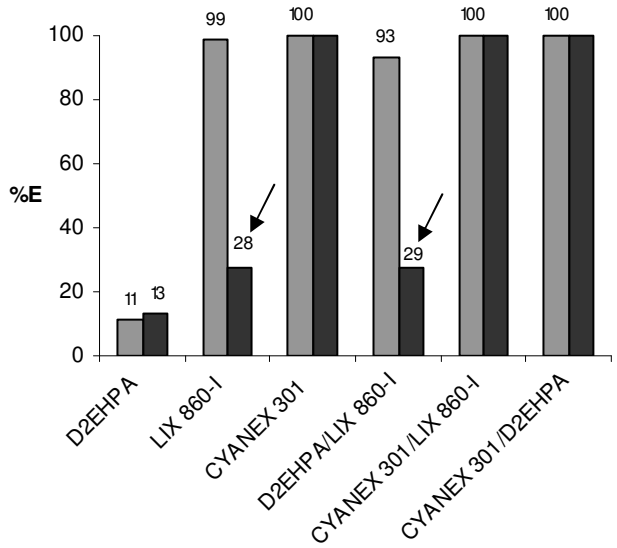


Figure 3-4. Extraction of Cu(II) with different extractants and its mixtures diluted in hexane (■) and 1-decanol (■)

Hexane

In the case of copper(II), synergistic effects are difficult to determine because of the good extraction performance already obtained with the separate use of LIX 860-I and CYANEX 301.

1-Decanol

Similar extraction efficiencies were obtained in 1-decanol as in hexane when CYANEX 301 was used as extraction reagent (either as separate extraction reagent or in a mixed extractant system). The presence of 1-decanol did also not affect the extraction performance of D2EHPA. On the other hand, the mixture of D2EHPA/LIX 860-I showed only poor extraction behaviour for copper(II) if 1-decanol was used as diluent. This was also the case for the separate use of LIX 860-I (see arrows). As mentioned already in

paragraph 3.2.1.1, the extraction efficiency of LIX 860-I for copper(II) is lower in electron-donor diluents than in non-polar hydrocarbons. Consequently, the weak results with LIX 860-I in 1-decanol also affected the extraction of copper(II) with a mixture of LIX 860-I and D2EHPA.

3.2.1.3. Influence of the addition of acetate ions to the aqueous phase

The same extraction procedures of paragraph 3.2.1.1 and 3.2.1.2 were repeated in the presence of 0.25 mol.L^{-1} acetate ions in the aqueous phase. The results in hexane and 1-decanol are shown in Figure 3-5 and are compared with the previous results. The extraction data in the presence of acetate ions and corresponding equilibrium pH values are included in Annex B (Table B-1).

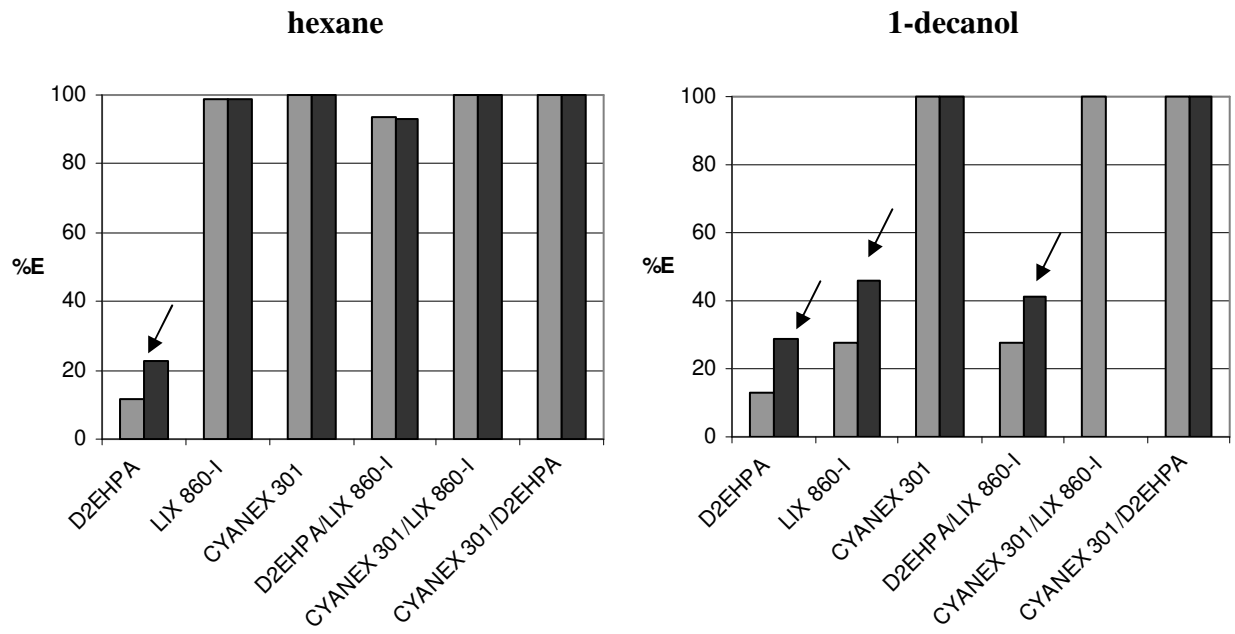


Figure 3-5. Influence of acetate ions on the extraction of Cu(II) with different extractants diluted in hexane and 1-decanol.
Without acetate (■), with 0.25 mol.L^{-1} acetate (■)

When the addition of acetate ions is taken into consideration, only a small increase of the extraction efficiency of copper(II) has been observed for D2EHPA in hexane and

1-decanol and for LIX 860-I and its mixture with D2EHPA in 1-decanol (see arrows). In the case of the other extractants, this effect is rather limited because of the very good extraction efficiencies already obtained under regular extraction circumstances.

The extraction percentage of copper(II) with a mixture of CYANEX 301 and LIX 860-I diluted with 1-decanol and in the presence of acetate ions is not presented in Figure 3-5 because of the formation of a very stable emulsion during shaking. Therefore no analysis could be performed.

3.2.2. Nickel(II)

3.2.2.1. Influence of the type of solvent (in the absence of acetate ions)

The extraction properties of nickel(II) are completely different compared to the previous heavy metal ion copper(II), which is preferentially extracted by most acidic extraction agents. The extraction results of nickel(II) with D2EHPA, LIX 860-I and CYANEX 301 are displayed in Figure 3-6. The extraction data and corresponding equilibrium pH values are included in Annex B (Table B-2).

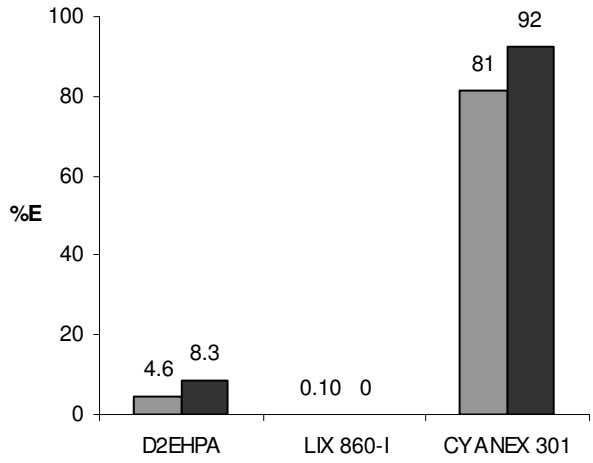


Figure 3-6. Extraction of Ni(II) with different extractants diluted in hexane (■) and 1-decanol (■)

Hexane

More difficulties were encountered in the case of nickel(II) extraction as compared to copper(II). With D2EHPA and LIX 860-I, very low extraction percentages were obtained. Only CYANEX 301 showed a good efficiency for the extraction of nickel(II) in hexane in the absence of acetate ions. However, Ni(II)-CYANEX 301 complexes in inert diluents are very stable and decomplexation is only rendered effectively when modifiers are added to the organic phase (see also Chapter 5) [3_18]. Hence, the application of the dithiosubstituted organophosphinic acid in hexane is not a useful procedure.

1-Decanol

A small increase in extraction percentages was found for D2EHPA and CYANEX 301. The nickel ion, with a coordination number of 6, tends to retain several water molecules in the first coordination sphere (see also paragraph 2.2.5). Higher alcohols are likely to have a greater ability to replace the water molecules than the present neutral extractants [3_16]. Consequently, the interaction of the diluent with the nickel complex is much greater than with the extractant, which is favourable for the extraction process.

3.2.2.2. Synergism (in the absence of acetate ions)

The extraction results of nickel(II) with D2EHPA, LIX 860-I, CYANEX 301 and its respective mixtures in hexane and 1-decanol are shown in Figure 3-7. The extraction data and corresponding equilibrium pH values are included in Annex B (Table B-2).

Hexane

A marked synergistic effect was found for the extraction of nickel(II) with a mixture of LIX 860-I and D2EHPA diluted in hexane (see arrow). The extraction percentage obtained with the mixture of these exctractants (34%) was higher than the sum of the extraction percentages obtained if both extractants are used separately (D2EHPA: 4.6% and LIX 860-I: 0.1%). In fact, when D2EHPA is combined with a hydroxyoxime, the pH isotherms shift to lower pH regions. This enables the performance of the extraction at lower pH values (see also Figure 2-18).

Combining CYANEX 301 with LIX 860-I or D2EHPA does not result in a synergistic effect.

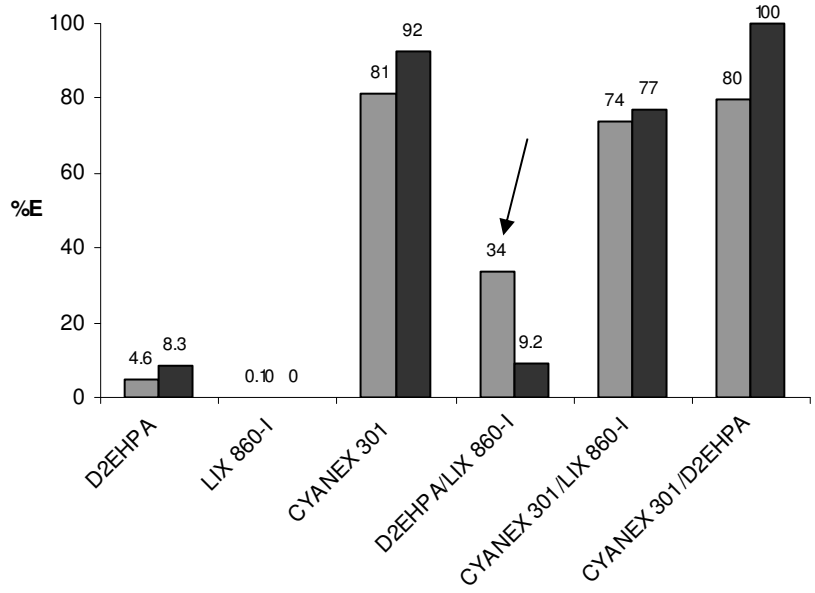


Figure 3-7. Extraction of Ni(II) with different extractants and its mixtures diluted in hexane (■) and 1-decanol (■)

1-Decanol

In the case of a mixture of LIX 860-I and D2EHPA, the presence of the higher alcohol does not improve the extraction. Furthermore, no synergistic effect is present in 1-decanol. This different extraction behaviour can be explained by the interactions between the hydroxyoxime and 1-decanol as discussed in paragraph 3.2.1.1.

3.2.2.3. Influence of the addition of acetate ions to the aqueous phase

The extraction procedures of paragraph 3.2.2.1 and 3.2.2.2 were repeated in the presence of 0.25 mol.L^{-1} acetate ions in the aqueous phase. The results in hexane and 1-decanol are shown in Figure 3-8 and are compared with the extraction results of nickel(II) without acetate. The extraction data in the presence of acetate ions and corresponding equilibrium pH values are included in Annex B (Table B-2).

The presence of acetate anions in the aqueous solution resulted into major improvements of most extraction efficiencies. The extraction percentage of nickel(II) was most affected when D2EHPA, LIX 860-I or a mixture of D2EHPA and LIX 860-I was used in the extraction procedure (see black arrows). In fact, the extraction of nickel(II) is very pH dependent (see also pH isotherms displayed in Figure 2-16). At pH 5.0, a (Na, H)Ac buffer is formed which results in an improved extraction efficiency, especially for nickel(II), which is only extracted at a higher pH level (4.5 -5.0) compared to copper(II) (pH 3.0) with most of the extractants used. The presence of acetate did not extremely affect the extraction of nickel(II) with CYANEX 301 because CYANEX 301 is able to extract many metal ions at a lower pH compared to the other extractants [3_13].

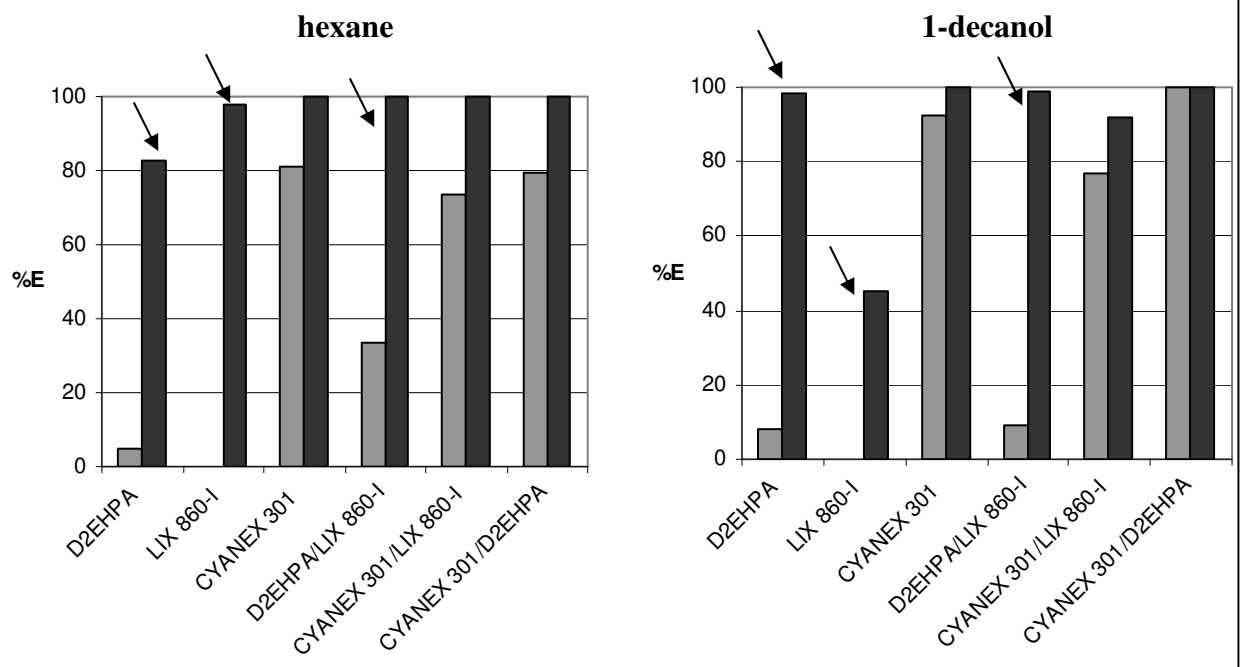


Figure 3-8. Influence of acetate ions on the extraction of Ni(II) with different extractants diluted in hexane and 1-decanol.
Without acetate (■), with 0.25 mol.L^{-1} acetate (■)

In a further study, the concentration of acetate was increased from 0 to 0.50 mol.L^{-1} to define the optimal concentration of acetate ions in the aqueous solution (see Figure 3-9). All nickel(II) solutions had an initial pH of 5.0.

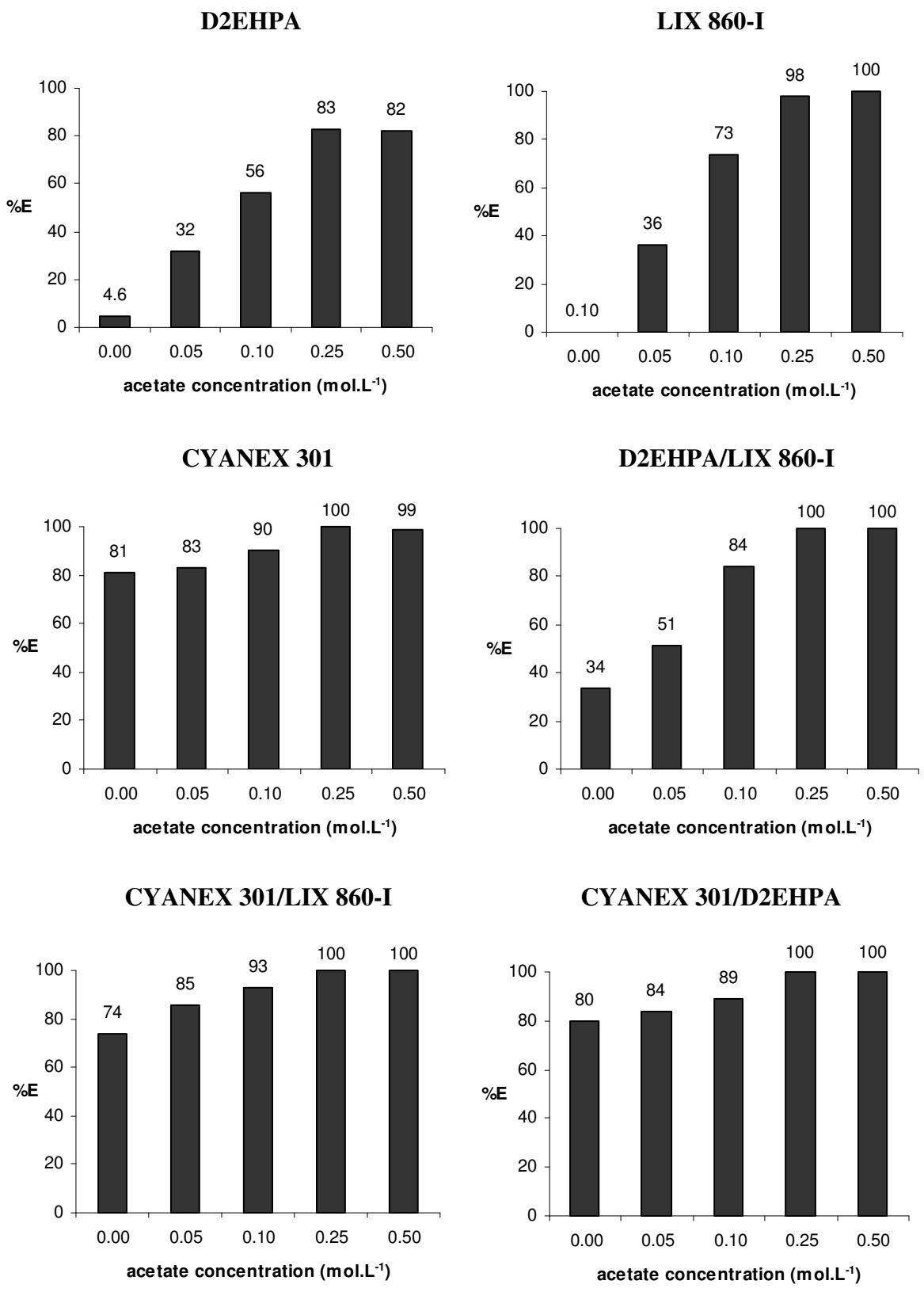


Figure 3-9. Influence of the concentration of acetate ions on the extraction of Ni(II) with different extractants diluted in hexane

Increasing concentrations of acetate ions improved the extraction ability of nickel(II) for each extractant and combinations of extractants as shown in Figure 3-9. Extraction percentages and equilibrium pH values are shown in Annex B (Table B-3). The highest improvements were found when at least 0.25 mol.L^{-1} acetate was added to the aqueous phase. By increasing the concentration of acetate in the aqueous phase, higher buffer capacities were reached at an initial pH of 5.0 and extraction of nickel(II) could take place at a constant pH level. The effect of the buffer capacity of the (Na, H) acetate system is also illustrated in Figure 3-10.

The liquid-liquid extractions of nickel with D2EHPA in the presence of different concentrations of acetate (see Figure 3-9) are compared with the results obtained with a pH adjustment control. Equal volumes (200 mL) of the organic phase containing 0.250 mol.L^{-1} D2EHPA in hexane and an aqueous phase of 0.0500 mol.L^{-1} Ni were rapidly stirred, and the pH was adjusted by small additions of NaOH. A contact time of 15 minutes was allowed between each pH adjustment although a constant pH was usually reached after approximately 2 minutes.

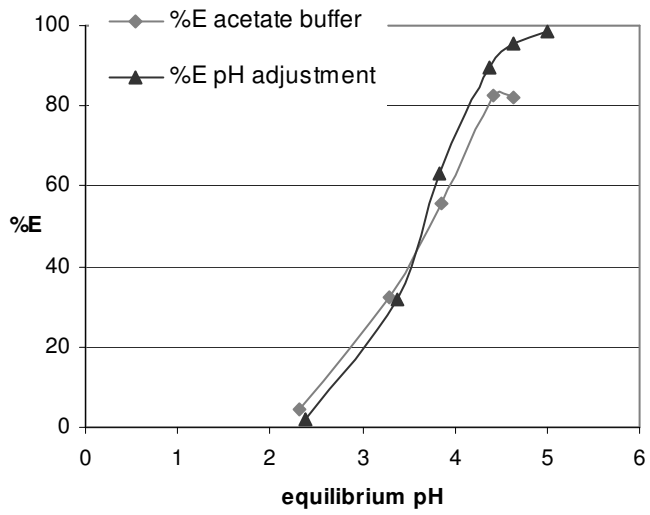


Figure 3-10. Comparison between a pH adjustment control and the addition of acetate buffer on the extraction efficiency of nickel(II) with D2EHPA

Figure 3-10 shows that the same curvature was obtained in the presence of acetate buffer or with a pH adjustment control. Although at a higher equilibrium pH, the extraction curve tended to remain at a lower extraction level in the presence of the (Na, H) Ac system.

The results discussed above have shown that acetate ions improve the extraction efficiency of nickel(II) during liquid-liquid extraction experiments. The effect of acetate in Supported Liquid Membranes is however not necessarily comparable with the effect in liquid-liquid extractions. SLM lab-scale experiments with nickel(II) and LIX 860-I or D2EHPA as extractants have shown that the presence of acetate can also have a deleterious effect upon the transport of nickel(II) [3_19]. The reason for this different behaviour is however not clear and was only investigated in the case of nickel(II) extraction.

3.2.3. Cobalt(II)

3.2.3.1. Influence of the type of solvent (in the absence of acetate ions)

The extraction performance of D2EHPA, LIX 860-I and CYANEX 301 for cobalt(II) extraction is shown in Figure 3-11. The extraction data as well as the equilibrium pH values are presented in Annex B, Table B-4.

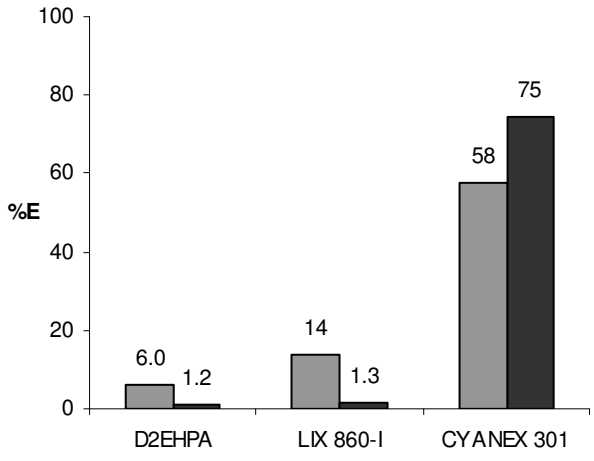


Figure 3-11. Extraction of Co(II) with different extractants diluted in hexane (■) and 1-decanol (■)

Hexane

In general, poor extraction results were obtained when hexane was used as diluent. With D2EHPA and LIX 860-I, extraction percentages of 6.0% and 14% were obtained, respectively. In the presence of CYANEX 301, 58% of the initial cobalt(II) concentration in the aqueous phase was extracted.

1-Decanol

The extraction of cobalt(II) with D2EHPA and LIX 860-I was even lower in 1-decanol compared to the extraction results obtained in hexane. Only CYANEX 301 showed a different behaviour in 1-decanol (small increase).

In literature [3_17], it is mentioned that a hydroxyl-containing diluent can interact with a cobalt-D2EHPA complex (tetrahedral symmetry in inert diluents) and convert it into an octahedral symmetry through the coordination of the alcohol molecules with the metal. Although the lower extraction percentage obtained with D2EHPA in 1-decanol infers that octahedral cobalt(II)-D2EHPA complexes are more difficult to achieve. In the case of LIX 860-I, also a lower extraction efficiency was obtained for cobalt(II) in the presence of 1-decanol as compared to hexane. The same trend was also observed for copper(II) and nickel(II) and can be explained by extractant-diluent interactions as already mentioned in paragraph 3.2.1.1.

3.2.3.2. Synergism (in the absence of acetate ions)

The results of the extraction studies of cobalt(II) with mixtures of extractants in hexane and 1-decanol are depicted in Figure 3-12 and are compared with the extraction results obtained with the separate use of these extraction reagents. The extraction data and the equilibrium pH values are listed in Annex B, Table B-4.

Hexane

In the case of the mixtures of extractants containing CYANEX 301, the extraction efficiency of cobalt(II) decreased compared to the separate use of CYANEX 301 in the liquid-liquid extraction procedure. The reason for this phenomenon is not clear. Normally, it would

be expected that at least the extraction percentage of CYANEX 301 is achieved. In the case of cobalt(II), the mixtures of extractants exhibit however a deleterious effect on its extraction efficiency.

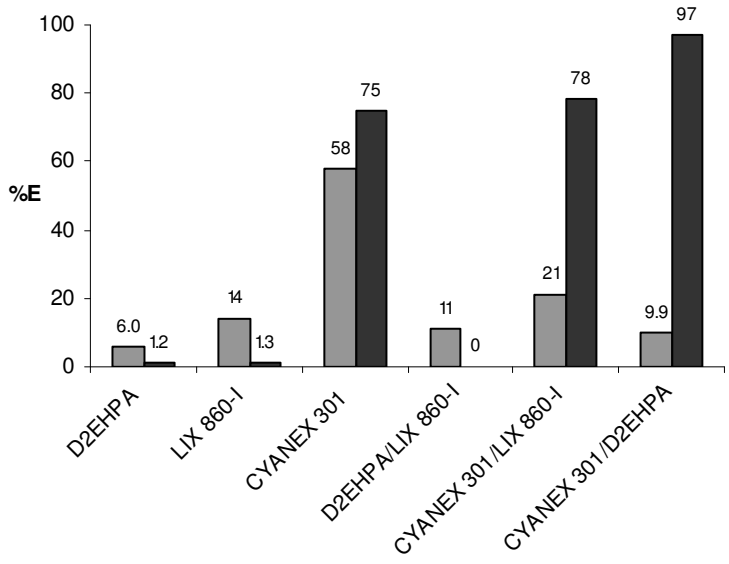


Figure 3-12. Extraction of Co(II) with different extractants and its mixtures diluted in hexane (■) and 1-decanol (■)

1-Decanol

Different extraction results were obtained with the mixtures of the extractants in 1-decanol compared to hexane. In the presence of CYANEX 301 in the extractant mixture, an increase of the extraction percentage was noticed for cobalt(II) in 1-decanol compared to hexane. On the other hand, with a mixture of D2EHPA and LIX 860-I, no extraction was obtained at all in 1-decanol. The lower extraction results in the presence of LIX 860-I and 1-decanol can be declared by the diluent-extractant interactions, which are expected to be minimal in the case of CYANEX 301.

3.2.3.3. Influence of the addition of acetate ions to the aqueous phase

The extraction results of cobalt(II) in the presence of acetate ions are compared with the results obtained without acetate in Figure 3-13. The extraction data and the equilibrium pH values are mentioned in Annex B, Table B-4.

The addition of acetate ions had a remarkable effect on the extraction of cobalt(II) (as was also the case for nickel(II)). In the presence of D2EHPA and LIX 860-I, this effect was most pronounced, except for the extraction of cobalt(II) with LIX 860-I in 1-decanol. In fact, the extraction of cobalt(II) is as pH dependent as the extraction of nickel(II) as shown in the pH-isotherms in Figure 2-16.

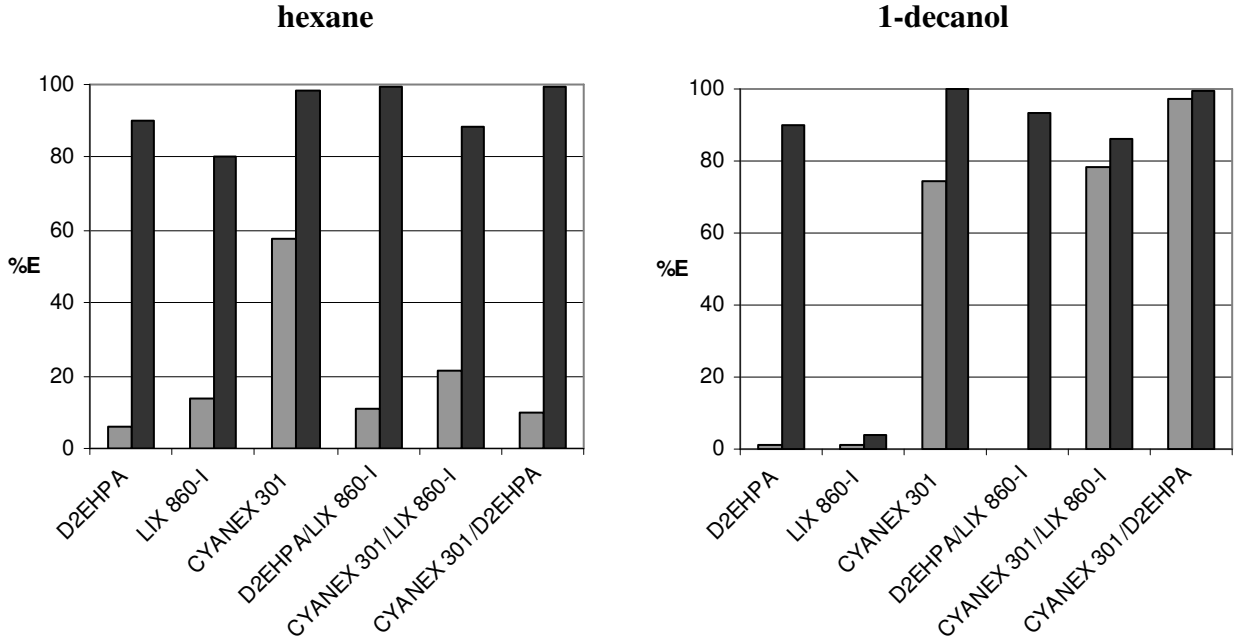


Figure 3-13. Influence of acetate ions on the extraction of Co(II) with different extractants diluted in hexane and 1-decanol. Without acetate (■), with 0.25 mol.L^{-1} acetate (■)

Different ligands with a hydrophobic-hydrophilic molecular structure were evaluated for the extraction of cobalt(II) with D2EHPA and LIX 860-I in hexane for a further

illustration of the pH influence. The different ligands were added to the aqueous phase containing 0.0500 mol.L^{-1} Co (II) (see also Annex B, Table B-5).

Higher extraction efficiencies were observed depending upon the chain length of the hydrophobic part of the ligand, as shown in Figure 3-14. Increasing the polarity of the ligand affected the extraction in a negative way. When lactate [$CH_3CHOHCOO^-$] was added to the aqueous phase, a lower extraction result was reached than with propionate [$CH_3CH_2COO^-$]. The results obtained are in agreement with the pK_a values of the corresponding acids, which are given in Table 3-1 [3_20]. The corresponding salt of a weaker acid added to the aqueous phase improved the extraction efficiency. A further illustration of the pH influence is shown in Figure 3-15.

Table 3-1. pK_a values of corresponding acids [3_20]

Acid	pK_a value
Formic acid	3.745
Acetic acid	4.757
Propionic acid	4.874
Butanoic acid	4.981
Lactic acid	3.854

The results obtained with the different aqueous ligands are now displayed in function of the equilibrium pH. A higher pH is beneficial for cobalt(II) extraction. Only the results of lactic acid are not included in this Figure because of its different structure compared to the other aqueous ligands.

Figure 3-15 also shows that with a mixture of D2EHPA and LIX 860-I, the pH-isotherm is shifted to lower pH values. This enables cobalt(II) to be extracted at a lower pH.

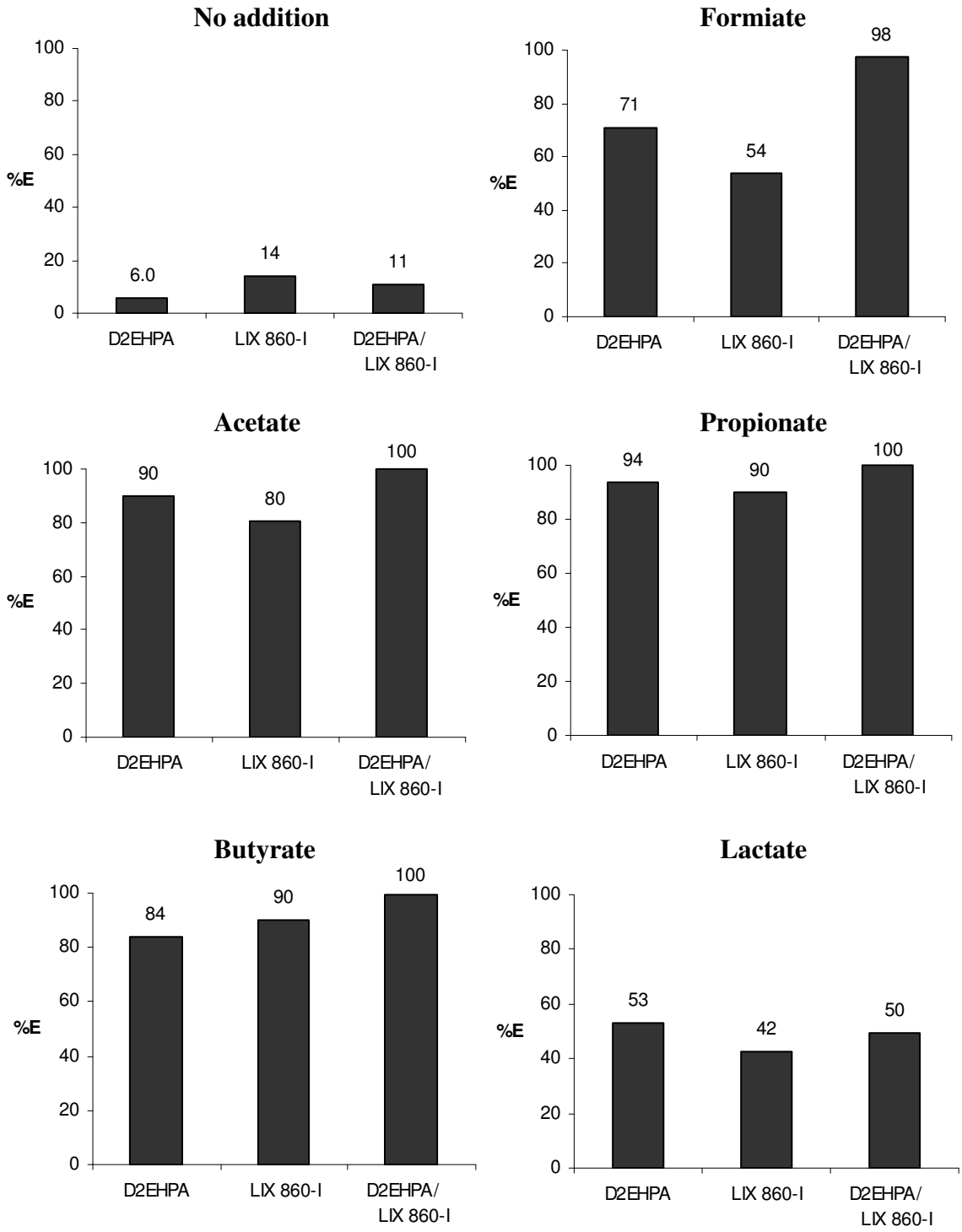


Figure 3-14. Influence of the type of ligand added to the aqueous phase on the extraction of cobalt(II).

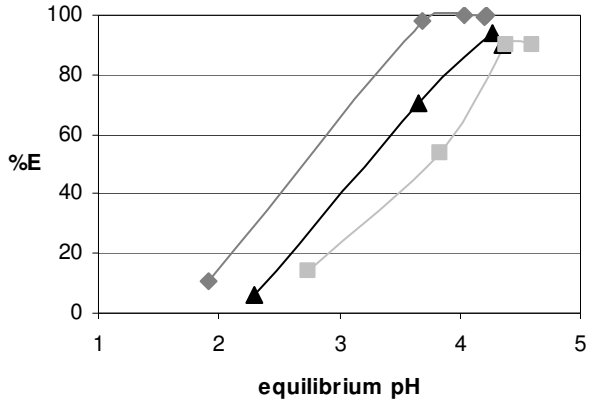


Figure 3-15. Extraction results of cobalt(II) expressed as a function of the equilibrium pH with D2EHPA (▲), LIX 860-I (■) and its mixture (♦)

3.2.4. Iron(III, II)

Both the divalent and trivalent oxidation state of iron is studied because major differences may exist in the respective extraction performance. The results will be discussed in the succeeding paragraphs.

3.2.4.1. Influence of the type of solvent (in the absence of acetate ions)

IRON(III)

The extraction results of iron(III) with D2EHPA, LIX 860-I and CYANEX 301 are shown in Figure 3-16. The corresponding equilibrium pH values are presented in Annex B, Table B-6.

Hexane

Fe(III) was extracted well with D2EHPA in hexane. Lower extraction results were obtained with LIX 860-I and CYANEX 301. In general, oxygen ligands have a high affinity for iron(III) [3_21]. D2EHPA - an organophosphorous acid derivative - is therefore very suitable

for iron(III) extraction (see also Table 1-4). This has been demonstrated by several authors [3_15, 3_22], even though also some problems have been described, viz. the decomplexation of the iron-D2EHPA complex. Nevertheless, the decomplexation problem can be solved by the correct use of stripping agent [3_23].

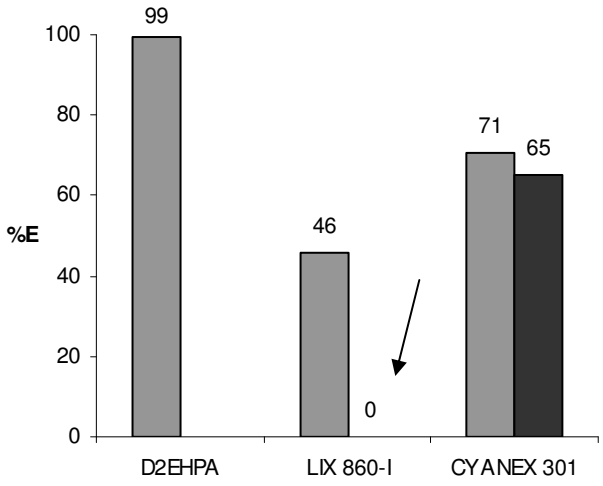


Figure 3-16. Extraction of Fe(III) with different extractants diluted in hexane (■) and 1-decanol (■)

1-Decanol

The extraction result of iron(III) with D2EHPA diluted in 1-decanol is not presented because of the formation of a very stable emulsion.

As can be seen from Figure 3-16, the presence of 1-decanol has an important effect on the extraction of iron(III) with LIX 860-I (see arrow). No extraction of iron(III) is obtained in 1-decanol. Interactions between the hydroxyoxime extraction reagent and diluent can explain the lower extraction efficiency of iron(III) in 1-decanol [3_17]. The type of diluent had no distinct effect on the extraction of iron(III) with CYANEX 301.

IRON(II)

The liquid-liquid extraction procedures in hexane and 1-decanol were repeated with iron(II) instead or iron(III). The extraction results of iron(II) with D2EHPA, LIX 860-I and

CYANEX 301 are shown in Figure 3-17. The corresponding equilibrium pH values are presented in Annex B, Table B-7.

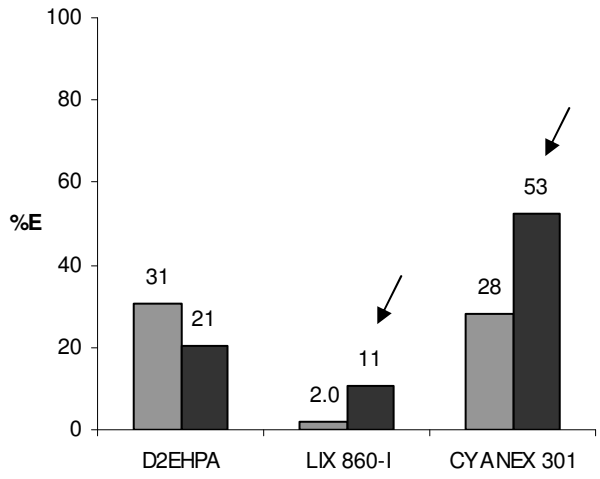


Figure 3-17. Extraction of Fe(II) with different extractants diluted in hexane (■) and 1-decanol (■)

Hexane

In general, it can be noticed that the extraction of iron(II) with D2EHPA, LIX 860-I and CYANEX 301 is much more difficult to achieve compared to the corresponding extraction of iron(III) in hexane.

1-Decanol

In the case of iron(II) and 1-decanol as diluent, a trend was noticed towards slightly higher extraction percentages, viz. LIX 860-I and CYANEX 301 (see arrows). Only D2EHPA deviated from this behaviour.

3.2.4.2. Synergism (in the absence of acetate ions)

In the case of iron(III, II), also mixtures of extractants were tested in order to determine if synergistic effects occur during the extraction of iron. The results are presented in the succeeding paragraphs.

IRON (III)

The extraction results of iron(III) in hexane and 1-decanol as diluent are shown in Figure 3-18. The equilibrium pH values are included in Annex B, Table B-6.

Hexane

In the presence of D2EHPA in the extractant mixture, no synergism could be determined because of the already good extraction performance of D2EHPA alone. Also with the extractant mixture of CYANEX 301 and LIX 860-I, no marked improvements were observed.

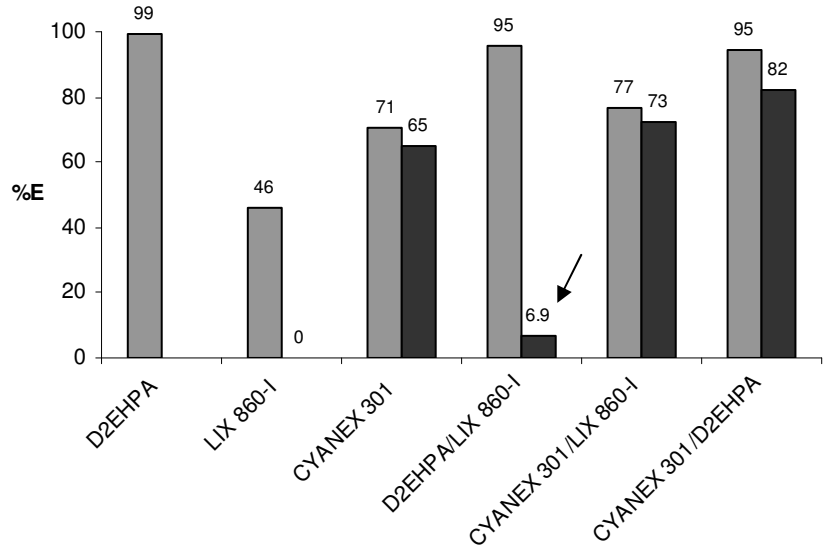


Figure 3-18. Extraction of Fe(III) with different extractants and its mixtures diluted in hexane (■) and 1-decanol (■)

1-Decanol

In general, no substantial differences were obtained between the extraction results of the mixtures of the extractants in 1-decanol compared to a non-polar solvent, except for the mixture of D2EHPA and LIX 860-I (see arrow). Nearly no extraction of iron(III) was determined with 1-decanol as diluent. The difference in extraction behaviour in 1-decanol compared to hexane can be due to diluent-extractant interactions, which are also affecting the extraction of iron(III) when LIX 860-I is used separately as extraction reagent. If D2EHPA also affects the extraction behaviour of iron(III) with the extractant mixture in 1-decanol cannot be deduced from the above results due to the formation of a very stable emulsion when D2EHPA is used separately as extraction reagent.

IRON(II)

The extraction results obtained with iron(II) and mixtures of extractants are displayed in Figure 3-19. Equilibrium pH values are included in Annex B, Table B-7.

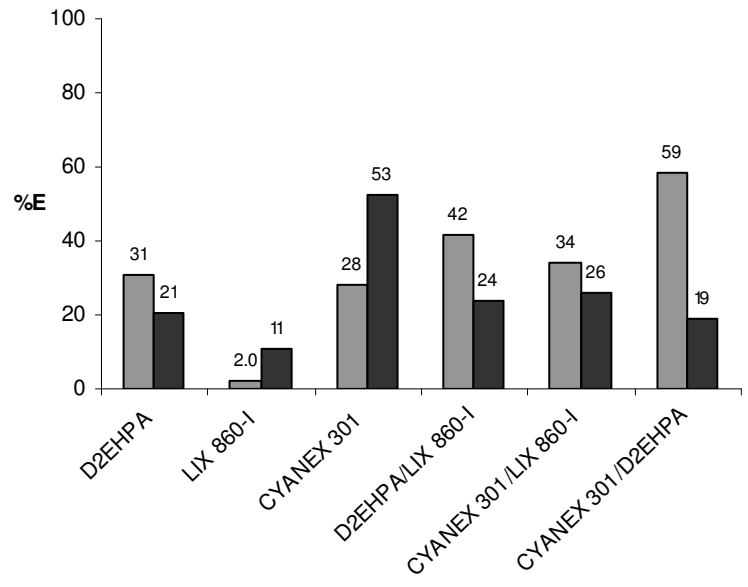


Figure 3-19. Extraction of Fe(II) with different extractants and its mixtures diluted in hexane (■) and 1-decanol (■)

Hexane

No profound synergistic effects were determined for Fe(II) with the mixtures of the extractants. Only in the case of D2EHPA/LIX 860-I (42%), the extraction percentage was higher than the sum of each extractant independently (D2EHPA: 31% and LIX 860-I: 2.0%). However, this increase is rather limited.

1-Decanol

There was a general trend towards higher extraction efficiencies when each extractant operated independently (except for D2EHPA), this in contrast to the mixed extractant systems. In general, a decrease in extraction percentages was noticed for the different mixtures compared to hexane, the effect being most pronounced for the mixture CYANEX 301/D2EHPA. In 1-decanol, no synergism was determined for the mixed extractant systems.

3.2.4.3. Influence of the addition of acetate ions to the aqueous phase

IRON(III)

The results in the presence of acetate ions are compared with the previous discussed results in Figure 3-20. Equilibrium pH values are included in Annex B (Tables B-6).

The extraction of iron(III) in hexane is not influenced by the presence of acetate ions in the aqueous phase. The extractions of iron(III) were performed at lower pH values (pH 1.5) compared to the other metal ions. At this low pH value, no (Na, H) Ac buffer is present (pK_a=4.757).

In 1-decanol, the extractions of iron(III) with LIX 860-I and with a mixture of D2EHPA and LIX 860-I were affected by the presence of acetate ions in the aqueous phase (see arrows). With LIX 860-I diluted in 1-decanol, no iron(III) was extracted in the absence of acetate ions.

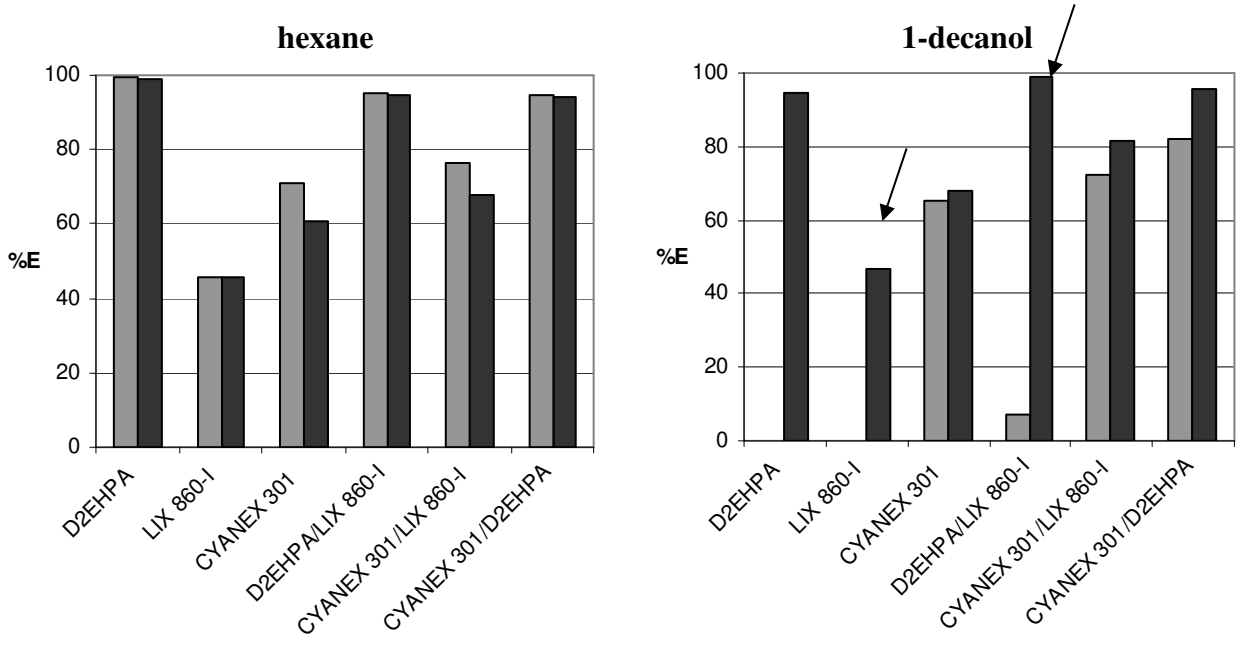


Figure 3-20. Influence of acetate ions on the extraction of Fe(III) with different extractants diluted in hexane and 1-decanol. Without acetate (■), with 0.25 mol.L^{-1} acetate (■)

The addition of the aqueous phase ligands improved the extraction. The same tendency was found for the mixture of D2EHPA and LIX 860-I. In the case of D2EHPA operating independently, no conclusion could be made since no analysis could be performed in the absence of acetate ions due to emulsion formation. The very fact that the increased extraction efficiency of iron(III) with LIX 860-I and its mixture with D2EHPA cannot be explained on the basis of the presence of a buffering agent proves that the latter is not always the reason of the improved extraction efficiencies as shown in the extraction processes of iron(III) in 1-decanol.

IRON(II)

The influence of the addition of acetate ions to the aqueous phase on the extraction behaviour of iron(II) is shown in Figure 3-21 (see also Annex B, Table B-7).

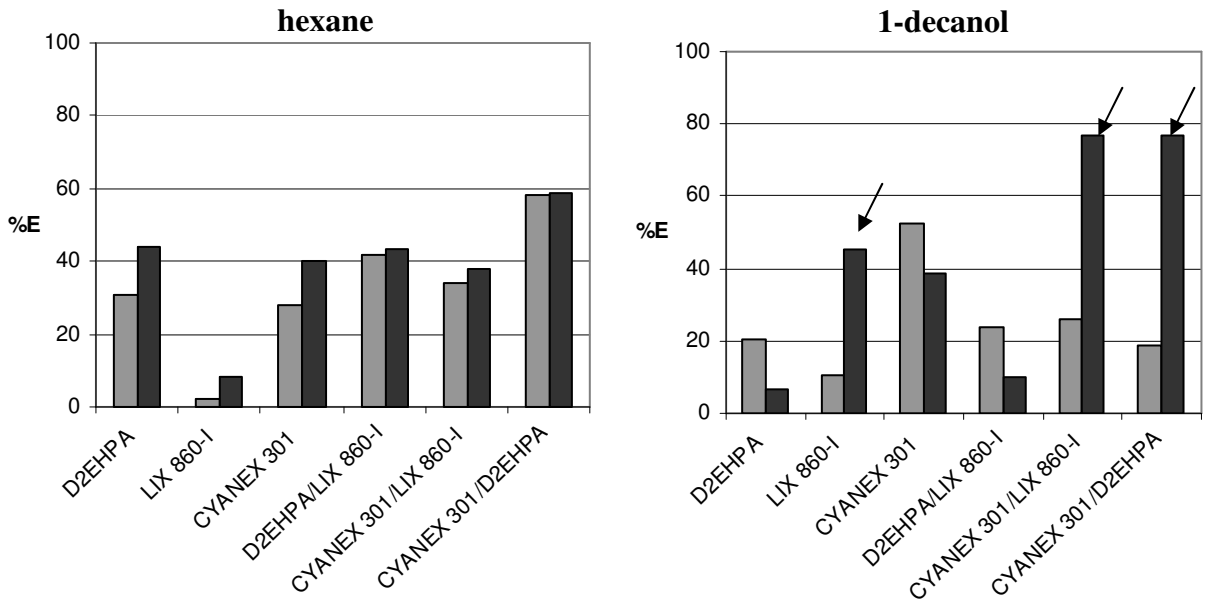


Figure 3-21. Influence of acetate ions on the extraction of Fe(II) with different extractants diluted in hexane and 1-decanol.
Without acetate (■), with 0.25 mol.L^{-1} acetate (■)

The presence of acetate ions did also not have a major effect on the extraction of iron(II) in hexane. However, in 1-decanol, more fluctuations were noticed. In the case of LIX 860-I and the mixtures CYANEX 301/LIX 860-I and CYANEX 301/D2EHPA, higher extraction percentages were obtained (see arrows). In the other cases, rather a decrease was noticed. Again, the increased extraction efficiencies cannot be explained on the basis of the presence of a buffering agent because the extractions were performed at a pH of 1.0.

3.2.5. Magnesium(II)

3.2.5.1. Influence of the type of solvent (in the absence of acetate ions)

Extraction results of magnesium(II) with D2EHPA, LIX 860-I and CYANEX 301 are shown in Figure 3-22. The corresponding equilibrium pH values are included in Annex B, Table B-8.

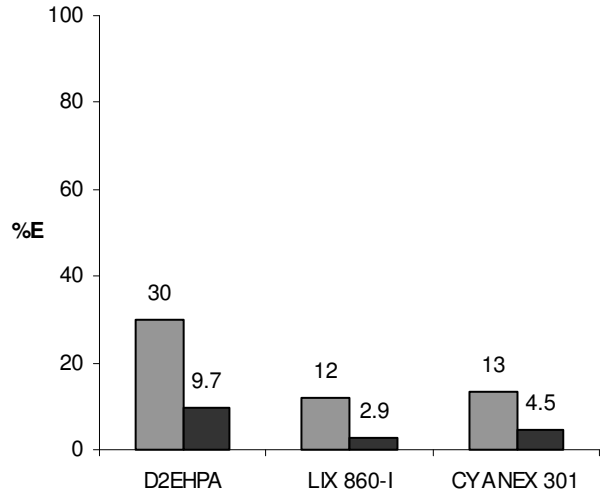


Figure 3-22. Extraction of Mg(II) with different extractants diluted in hexane (■) and 1-decanol (■)

As shown in Figure 3-22, magnesium(II) is only poorly extracted by the applied extractants if hexane is used as diluent. D2EHPA showed the highest extraction performance towards magnesium(II).

In 1-decanol as diluent, the results were even lower as compared to hexane. In fact, nearly no extraction was obtained of magnesium(II) in 1-decanol with the different extractants.

3.2.5.2. Synergism (in the absence of acetate ions)

The mixed extractant systems were also investigated for the extraction of magnesium(II). The extraction results are shown in Figure 3-23. Extraction data and equilibrium pH values are included in Annex B, Table B-8.

The mixed extractant systems diluted in hexane did not improve the extraction efficiency of magnesium(II). Also with the mixtures of the extractants diluted in 1-decanol, the extraction efficiency of magnesium(II) was rather limited. In 1-decanol, the mixture of CYANEX 301 and D2EHPA (see arrow) showed the best extraction characteristics for magnesium(II). 39% extraction was obtained compared to 9.7% and 4.5% for the extractants D2EHPA and CYANEX 301, respectively, when used independently.

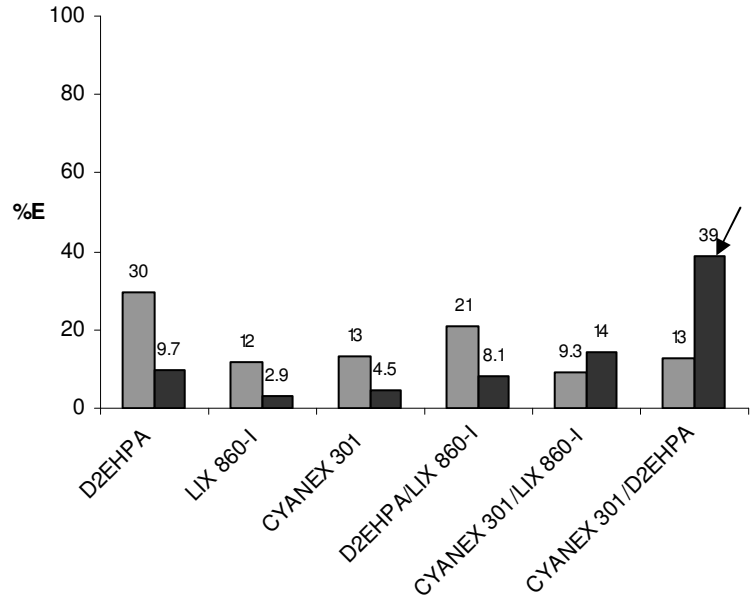


Figure 3-23. Extraction of Mg(II) with different extractants and its mixtures diluted in hexane (■) and 1-decanol (■)

3.2.5.3. Influence of the addition of acetate ions to the aqueous phase

In another set of experiments, acetate ions were added to the aqueous phase. The results of these extractions are compared with the extraction results obtained without acetate in Figure 3-24. Extraction data and equilibrium pH values are given in Annex B, Table B-8. The extraction result of the mixture of LIX 860-I and D2EHPA in 1-decanol in the presence of acetate ions is not presented because of the formation of a very stable emulsion during shaking. In the case of LIX 860-I alone – diluted in 1-decanol, no extraction of magnesium(II) was obtained in the presence of acetate ions.

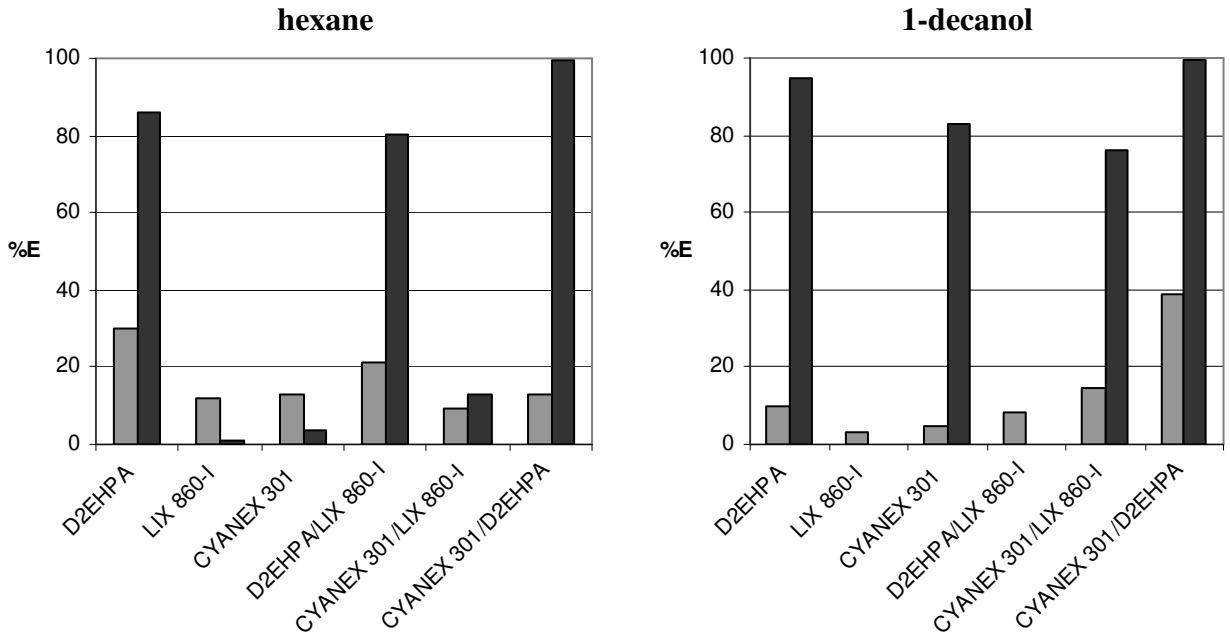


Figure 3-24. Influence of acetate ions on the extraction of Mg(II) with different extractants diluted in hexane and 1-decanol. Without acetate (■), with 0.25 mol.L^{-1} acetate (■)

Major extraction improvements were noticed when D2EHPA was present as ligand in the organic phase, either alone or in a mixed extractant system in the presence of acetate ions in the aqueous phase. The (Na, H) acetate buffer system maintains the pH at 5.0, which is favourable for the extraction of magnesium(II). This can also be observed from the pH-isotherms of D2EHPA, which are depicted in Figure 2-16. At pH values > 4.5, magnesium as well as calcium can be extracted by D2EHPA.

Acetate ions also improve the extraction performance of CYANEX 301, but only when 1-decanol is applied in the extraction process. The improved extraction efficiency cannot be attributed to the buffer effect of the (Na, H) acetate system alone, as in hexane no increase was observed in the presence of acetate ions. No improvement in the extraction efficiency of magnesium(II) was found with LIX 860-I (separate use).

3.2.6. Summary

The results obtained for the various metals show that a careful choice of extractant or mixtures of extractants and extraction circumstances (e.g. solvent, pH) is very important for a

successful operation. Mixtures of extractants can show synergistic effects, viz. nickel(II) extraction with LIX 860-I and D2EHPA. The extraction percentage of the mixture of the extractants was markedly higher than the sum of the extraction percentages obtained with each extractant independently.

Interactions of polar solvents, e.g. higher alcohols such as 1-decanol, with extractant molecules, viz. LIX 860-I, affect the extraction of copper(II), nickel(II), cobalt(II), iron(III) and magnesium(II) in a negative way. With the other extractant molecules, e.g. D2EHPA and CYANEX 301, interactions with the polar solvent can be expected to be rather moderate. Therefore, no general trend towards lower extraction efficiencies was observed with D2EHPA and CYANEX 301, this in contrast to the extraction results obtained with LIX 860-I in 1-decanol.

Besides the solvent, the pH also plays a major role in the extraction process of the metal ions. By adding a buffering agent, viz. (Na, H) acetate, the extraction efficiencies of some metal ions can be significantly increased. In the case of nickel(II), cobalt(II) and magnesium(II) extraction with D2EHPA and LIX 860-I, the pH must be kept high enough (pH 4.5-6.0) during the extraction process. Only CYANEX 301 deviates from this behaviour because it extracts metal ions at a lower pH.

In the case of iron(III, II) and sometimes magnesium(II), higher extraction results were reached in the presence of acetate ions which in particular cannot be explained on the basis of the presence of a buffering agent (experiments of iron(III) and iron(II) were performed at pH 1.5 and 1.0, respectively). Therefore, the metal-organic complexes are examined in depth in a further study by means of the FT-IR and UV-VIS spectra of the specific complexes. In the succeeding paragraphs, the FT-IR spectra (paragraph 3.3) as well as the UV-VIS absorption spectra (paragraph 3.4) of the metal-organic complexes will be discussed.

3.3. FOURIER-TRANSFORM INFRARED SPECTRA OF THE METAL-ORGANIC COMPLEXES

Fourier-Transform Infrared (FT-IR) is a useful tool to study any changes in complexation behaviour which are related to additives. Pure rotation gives rise to absorption in the microwave region. Molecular vibrations give rise to absorption bands throughout most of the infrared region of the spectrum.

In the succeeding paragraphs, the most profound changes in FT-IR spectra will be discussed for copper(II), nickel(II) and cobalt(II). Iron(III, II) and magnesium(II) spectra are not included because only minor differences in spectra or the occurrence of very broad bands were noticed. Furthermore, the discussion of the FT-IR spectra is limited to the spectra of D2EHPA and LIX 860-I because instability issues may influence the spectra obtained with CYANEX 301 [3_16]. The extraction of copper(II) and iron(III) with CYANEX 301 can involve the reduction of the metal ion to copper(I) and iron(II), respectively, and the accompanying oxidation of the ligand to the disulfide [$R_2P(S)$-S-S-$(S)PR_2$] [3_16].

3.3.1. Copper(II)

The introduction of acetate ions did not significantly affect the extraction efficiency of copper(II) ions. These findings received additional support from the FT-IR analysis of the metal-organic complexes.

Figure 3-25A shows the FT-IR spectrum of LIX 860-I dissolved in hexane in the range 1760-1520 cm^{-1}. Two bands appear at 1623 and 1584 cm^{-1}. The band at 1623 cm^{-1} is due to the C=N stretching vibration (for structure of LIX 860-I: see Figure 3-26) and the band at 1584 cm^{-1} is due to the ortho-substituted benzene ring vibration of the hydroxyoxime ligand [3_24]. Figure 3-25B and C respectively show the complexes formed with copper(II) in the absence and in the presence of 0.25 $mol.L^{-1}$ acetate in the aqueous phase. Figure 3-27 shows the FT-IR spectrum of acetic acid added to LIX 860-I diluted in hexane.

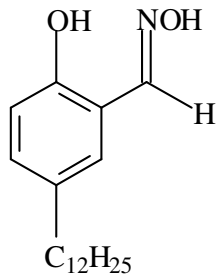


Figure 3-26. Structure of LIX 860-I

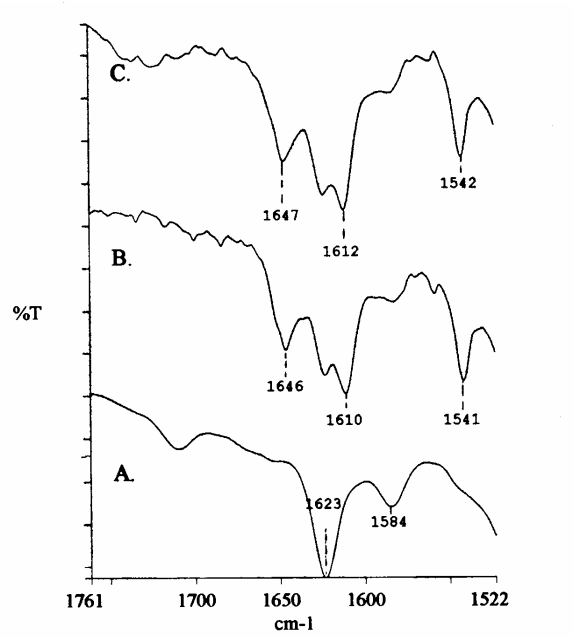


Figure 3-25. FT-IR spectrum of LIX 860-I (A) compared with Cu(II)-LIX 860-I complexes in hexane: (B) liquid-liquid extraction without acetate in aqueous phase, (C) liquid-liquid extraction in the presence of 0.25 mol.L^{-1} acetate in aqueous phase

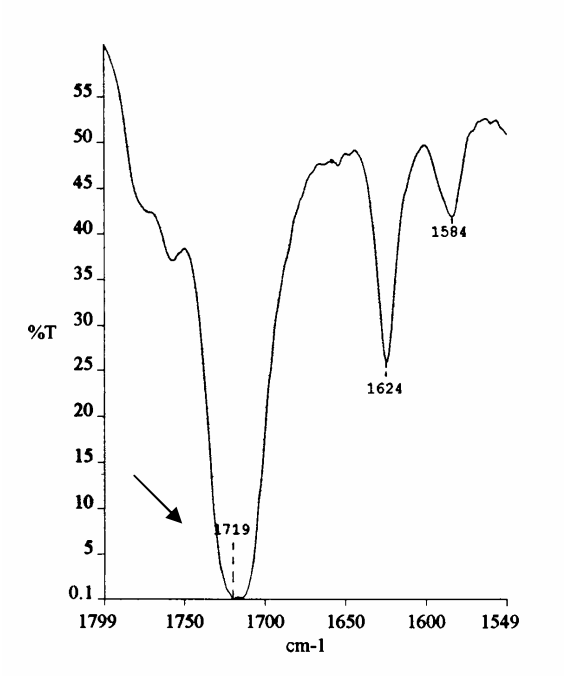


Figure 3-27. FT-IR spectrum of acetic acid added to LIX 860-I diluted in hexane

No differences were observed between spectra 3-25B and 3-25C and no band around 1700 cm^{-1} appeared in spectrum 3-25C that could be related to the carbonyl function of the acetate ions. In Figure 3-27, the broad band due to the carbonyl function is shown at 1719 cm^{-1} (see arrow) by adding acetic acid directly to the organic phase.

The FT-IR spectra of the copper(II) complexes formed with LIX 860-I in 1-decanol as diluent are shown in Figure 3-28.

The spectrum shown in Figure 3-28A is the result of a shaking experiment with copper(II) without extractant but in the presence of acetate in the aqueous phase, while spectra 3-28B and C were respectively obtained after shaking copper(II) with LIX 860-I without and in the presence of 0.25 $mol.L^{-1}$ acetate in the aqueous phase. In 1-decanol, the band from a carbonyl function appeared at 1710-1711 cm^{-1} - even when no extractant was present. This was not the case for hexane.

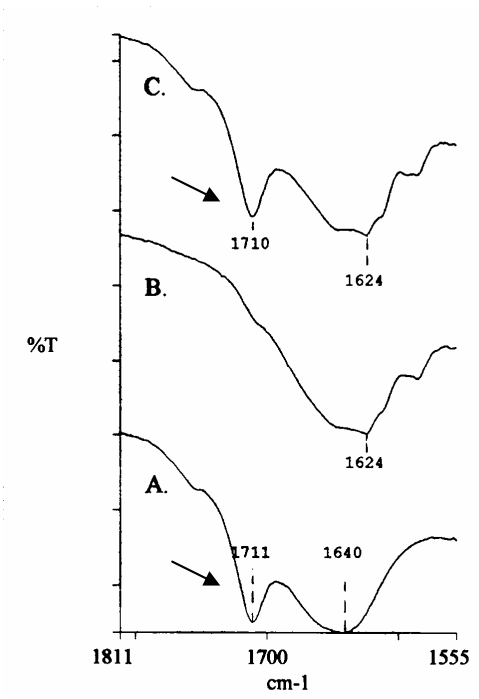


Figure 3-28. FT-IR spectra of organic phase in the case of Cu(II) extraction with LIX 860-I diluted in 1-decanol.
(A) without extractant and in the presence of 0.25 $mol.L^{-1}$ sodium acetate in aqueous phase,
(B) liquid-liquid extraction without acetate in aqueous phase,
(C) liquid-liquid extraction in the presence of 0.25 $mol.L^{-1}$ acetate in aqueous phase

The results discussed above reveal that acetate (most probably acetic acid) can migrate to the organic membrane phase even in the absence of an extractant when 1-decanol is used as diluent. However, no evidence was found that suggests any active role of acetate in the formation of the copper(II) complexes.

The FT-IR spectra with D2EHPA (structure see Figure 3-29) are not included because of the occurrence of the very broad band of the OH bending vibration around 1680 cm^{-1} [3_25].

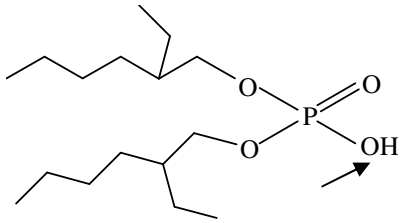


Figure 3-29. Structure of D2EHPA

3.3.2. Nickel(II)

In the case of nickel(II), very distinct improvements in the extraction performance of the different extractants were determined. Whether acetate also participates or not in the formation of the complexes was further investigated by inspection of the FT-IR spectra. In Figure 3-30, the FT-IR spectrum of the nickel(II)-LIX 860-I complex in hexane is shown and a comparison is made with the spectrum obtained from the extractant itself.

Figure 3-30 shows that spectra A and B are similar. The FT-IR spectrum 3-30C, on the other hand, showed new bands at 1647, 1612 and 1551 cm^{-1} comparable to the FT-IR spectrum of the copper(II) complex with LIX 860-I (Figure 3-25). The reason why spectrum 3-30B is not the same as spectrum 3-30C is because of a very low nickel(II) extraction obtained with LIX 860-I without (Na, H) Ac buffer (see also Figure 3-6).

Again, no band appeared around 1700 cm^{-1} in spectrum 3-30C. This would already mean that no acetate and/or acetic acid passes from the aqueous to the organic phase, in accordance with [3_8].

The FT-IR spectra with D2EHPA are again not included because of the very broad band of the OH bending vibration present around 1680 cm^{-1} [3_25].

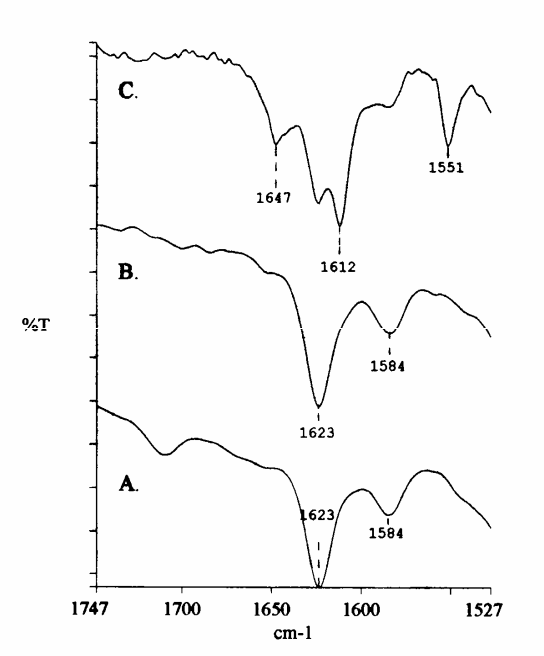


Figure 3-30. FT-IR spectrum of LIX 860-I (A) compared with
Ni(II)-LIX 860-I complexes in hexane:
(B) liquid-liquid extraction without acetate in aqueous phase,
(C) liquid-liquid extraction in the presence of 0.25 mol.L^{-1} acetate in aqueous phase

3.3.3. Cobalt(II)

In general, the extraction efficiency of cobalt(II) was influenced in the same way as observed for nickel(II) due to the presence of acetate in the aqueous phase. The FT-IR spectra are discussed hereafter.

In Figure 3-31, the FT-IR spectra are shown of the organic phases resulting from an extraction experiment of cobalt(II) with LIX 860-I diluted in hexane without and in the presence of acetate.

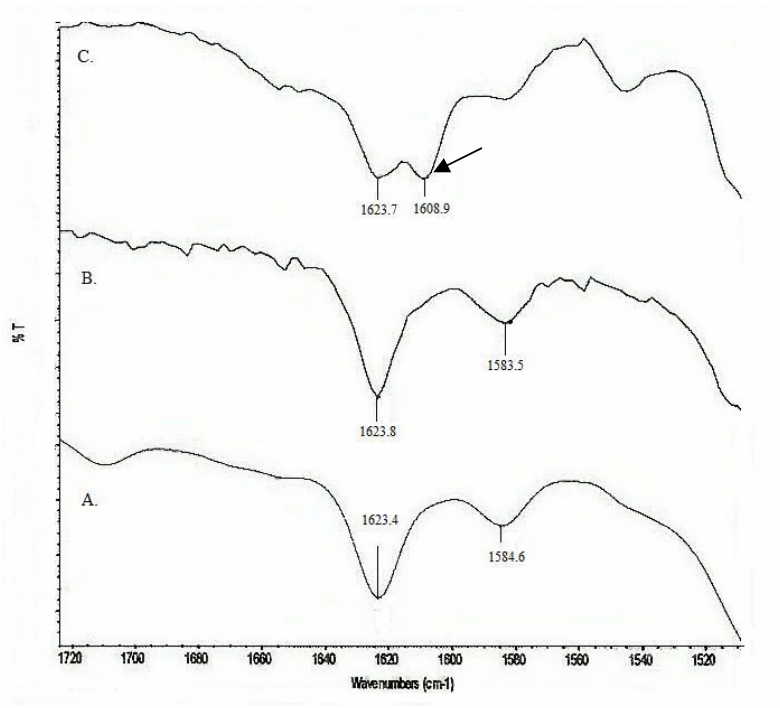


Figure 3-31. FT-IR spectrum of LIX 860-I (A) compared with Co(II)-LIX 860-I complexes in hexane:
(B) liquid-liquid extraction without acetate in aqueous phase,
(C) liquid-liquid extraction in the presence of 0.25 mol.L^{-1} acetate in aqueous phase

As can be noticed from Figure 3-31, a new band appeared in spectrum 3-31C at 1608.9 cm^{-1} (see arrow). In spectrum 3-31B, this band is again absent, as was also the case in the FT-IR spectrum of nickel(II) when no acetate ions were present in the aqueous phase during extraction. The difference between spectra 3-31B and C can again be explained by the presence of the (Na, H) Ac buffer, which improves the extraction. No band appeared at 1700 cm^{-1}, which infers that no acetate and/or acetic acid was present in the organic phase.

3.4. UV-VIS ABSORPTION SPECTRA OF THE METAL-ORGANIC COMPLEXES

Besides Fourier-Transform Infrared (FT-IR) spectra, UV-VIS absorption spectra are also useful to gain a better insight in the complexation characteristics of the different metal ions and to study any changes in complexation behaviour, which are related to additives or

mixed extractant systems. Electronic energy transitions normally give rise to absorption or emission in the ultraviolet and visible regions of the electromagnetic spectrum.

In the succeeding paragraphs, the most profound changes in UV-VIS absorption spectra will be discussed for copper(II), nickel(II) and cobalt(II). Iron(III, II) and magnesium(II) spectra are not included because only minor differences in spectra were noticed. The spectra of CYANEX 301 are again not included because of instability reasons [3_16].

3.4.1. Copper(II)

The introduction of acetate ions did not significantly affect the extraction efficiency of copper(II) ions. These findings received additional support from the FT-IR analysis of the metal-organic complexes. Also the UV-VIS absorption spectra showed no substantial shifts that could support any participation of acetate/acetic acid in the formation of the copper(II)-complexes. In the case of copper(II)-LIX 860-I complexes, no differences were observed. Therefore these spectra are not included. In the case of D2EHPA, it was difficult to interpret the difference between the absorption spectra because very broad bands were formed as shown in Figure 3-32. In Figure 3-32, the absorption spectra of the copper(II)-D2EHPA complexes in hexane are compared with the spectra obtained in 1-decanol. Figure 3-44a results from shaking experiments without acetate in the aqueous phase, while in Figure 3-44b acetate was added to the aqueous phase during the liquid-liquid extraction experiments.

Figure 3-32 shows that in the presence of acetate ions in the aqueous phase during a shaking experiment, a higher absorbance was achieved, which was due to a small increase of the extraction percentages. However, no indications were found that acetate also participates in the formation of the copper(II) complexes.

Copper(II), with electron configuration d^9, usually forms distorted tetrahedral and octahedral or square-planar complexes (see Table 1-3). In a diluent with electron-donor properties such as 1-decanol, the molecules of 1-decanol are able to coordinate to the central Cu^{2+} ion [3_25]. Therefore, a transformation of an approximately square planar configuration in inert diluents into a tetragonal or octahedral one in a chemically active diluent such as 1-decanol can take place.

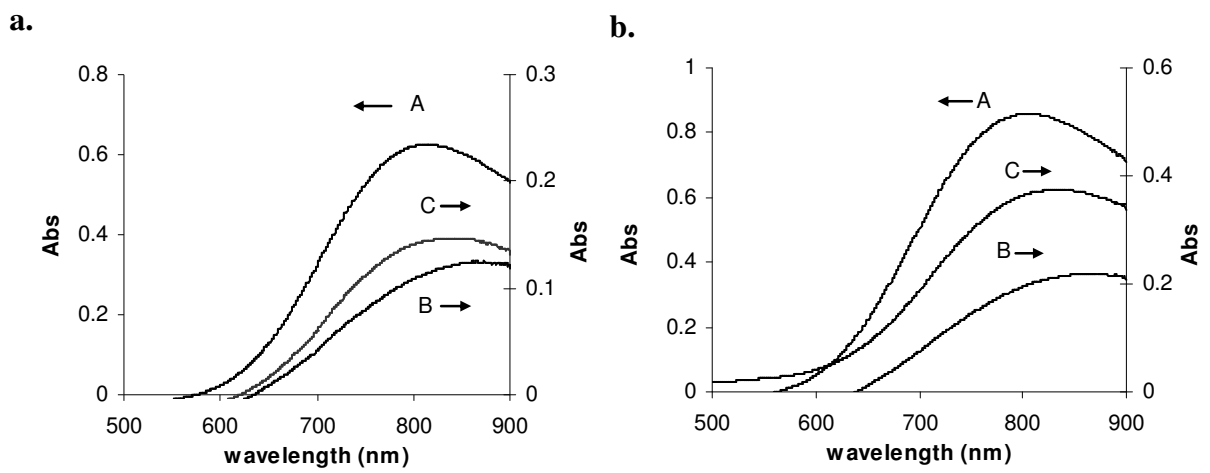


Figure 3-32. Absorption spectra of Cu(II) in the aqueous phase (A) compared with the Cu(II)-D2EHPA complex in hexane (B) and 1-decanol (C).

a. liquid-liquid extraction without acetate in aqueous phase,

b. liquid-liquid extraction in the presence of 0.25 mol.L^{-1} acetate in aqueous phase

3.4.2. Nickel(II)

The UV-VIS absorption spectra of the nickel(II)-organic complexes in hexane without and in the presence of sodium acetate in the aqueous phase are discussed in this paragraph. The VIS spectra obtained with D2EHPA are shown in Figure 3-33. The spectra were compared with the spectrum of Ni(II) in the aqueous phase.

The same absorption spectra have been obtained and therefore the same coordination geometry is suggested. Nickel(II), with the electron configuration d^8, can form different complexes, the main structural types being octahedral, tetrahedral and square planar (see Table 1-3). The nickel(II)-D2EHPA complex in hexane showed the characteristics of an octahedral complex, which was also true for the spectrum of the nickel ions in the aqueous phase [3_20]. This octahedral complex is expected to exhibit three spin-allowed transitions [3_27, 3_28] from the ground state $^3A_{2g}(F)$ to states $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$. In the spectrum of the nickel(II)-D2EHPA complex, the absorption bands at 24 938 cm^{-1} (400 nm) and 13 605 cm^{-1} (735 nm) can be assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition respectively. The third transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ was out of the working range of the Cary 100 Bio UV-Visible spectrophotometer but was expected in the

near-infrared region. In literature [3_28] a band was defined at 8300 cm^{-1} (1205 nm) as the third transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$. Because no shifts in absorption bands were observed, it may be stated that acetate/acetic acid does not participate in the formation of the nickel complexes what is in accordance with the results of infrared analysis.

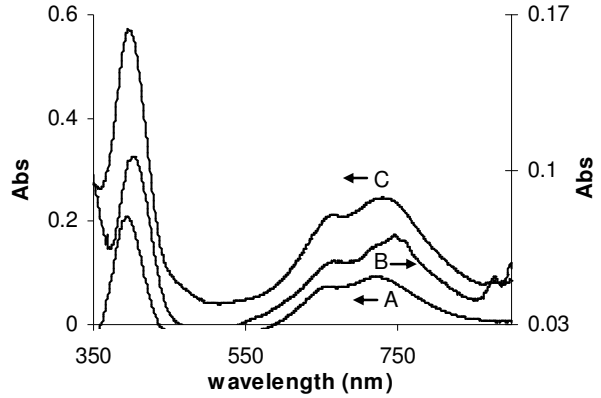


Figure 3-33. Comparison of absorption spectra of Ni(II) in the aqueous phase (A) and Ni(II)-D2EHPA complexes in hexane:
(B) liquid-liquid extraction without acetate in aqueous phase,
(C) liquid-liquid extraction in the presence of 0.25 $mol.L^{-1}$ acetate in aqueous

Also no shifts in absorption bands were observed for the extraction of nickel(II) with the mixed extractant system D2EHPA-LIX 860-I due to the presence of acetate ions. Figure 3-34 shows a part of the visible spectrum of the Ni(II)-D2EHPA-LIX 860-I complex compared to the performance of the extractants alone in both diluents and the spectrum of Ni(II) in the aqueous phase. All spectra of Figure 3-34 were obtained from extraction procedures with 0.25 $mol.L^{-1}$ acetate in the aqueous phase.

The spectrum of the Ni(II)-D2EHPA complex was not influenced by the nature of the diluent. In both cases, an octahedral coordination was observed. Interaction of the diluent with the extracted nickel complex however may occur by replacement of the coordinated neutral extractant molecules and/or water molecules [3_2, 3_17]. A small increase in the extraction efficiency of nickel(II) was observed with D2EHPA in 1-decanol (see Figure 3-6).

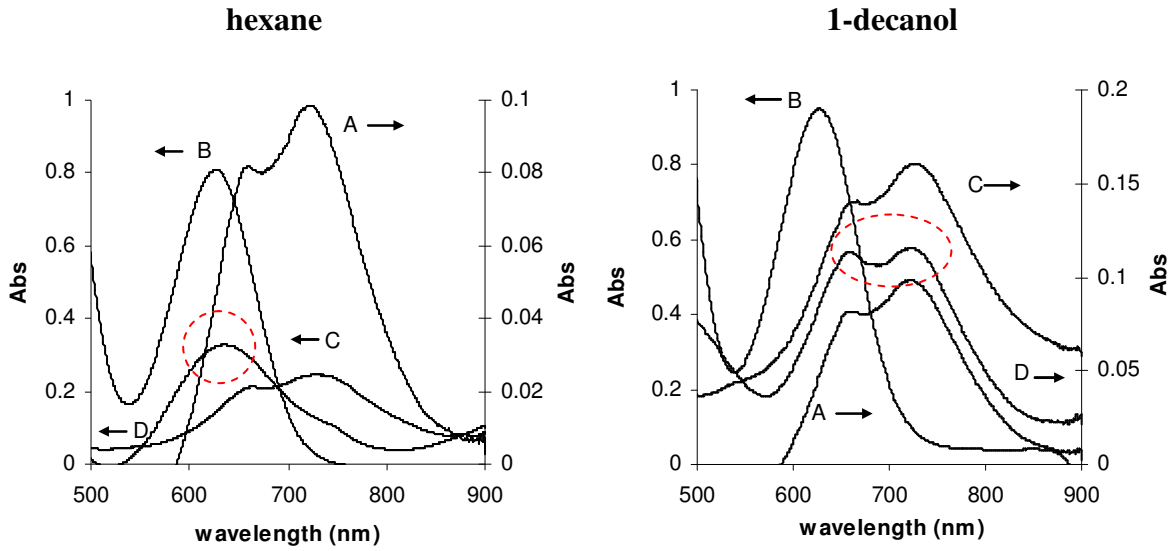


Figure 3-34. Absorption spectra of Ni(II) in the aqueous phase (A) compared with nickel(II) complexes of LIX 860-I (B), D2EHPA (C) and its mixture (D)

The spectrum of the Ni(II)-LIX 860-I complex was also showing the same curvature in both diluents but lower extraction percentages were obtained in 1-decanol compared to hexane (see also Figure 3-6). In this case, the diluent may interact with the extractant molecules and therefore exhibit a deleterious influence upon the extraction, as was also the case for copper(II) [3_17]. Investigation of the crystal structure of the bis(salicylaldoximato)nickel(II) complex indicated the formation of a slightly distorted planar geometry [3_29].

For the extraction of nickel(II) with a mixture of LIX 860-I and D2EHPA however, an improved extraction efficiency was observed in hexane and this seemed to be nonexistent in 1-decanol (see Figure 3-7). Therefore, a difference in absorption spectrum was expected. One extractant complexes the metal ion and neutralizes the charge while the second extractant serves to replace water molecules or to occupy free coordination sites. Whether LIX 860-I or D2EHPA is responsible for the solvatation is not clear. Also previous research [3_3, 3_30] showed contradictory statements about the active role of each extractant in the metal complex. In hexane, the spectrum of the nickel complex formed with LIX 860-I and D2EHPA tended more towards the spectrum of LIX 860-I. In 1-decanol, the same absorption spectrum was formed as in the case D2EHPA was used separately as extraction agent. Also the synergism between LIX 860-I and D2EHPA for the extraction of nickel(II) was not observed in

1-decanol (see also Figure 3-7). This can be due to the fact that a strong interaction already exists between the diluent and the metal complex, which prevents any interaction with the second extractant.

3.4.3. Cobalt(II)

Substantial shifts were found in the absorption spectra of cobalt(II) complexes when the complex was surrounded by a diluent with electron-donor properties such as 1-decanol compared to the results obtained in hexane. The greatest differences were found in the complexation of cobalt(II) with D2EHPA. In Figure 3-35, the spectrum of Co(II) in the aqueous phase (spectrum 3-35A) is compared with the spectra obtained in hexane (spectrum 3-35B) and 1-decanol (spectrum 3-35C) after shaking a cobalt(II) solution with D2EHPA with or without acetate ions in the aqueous phase.

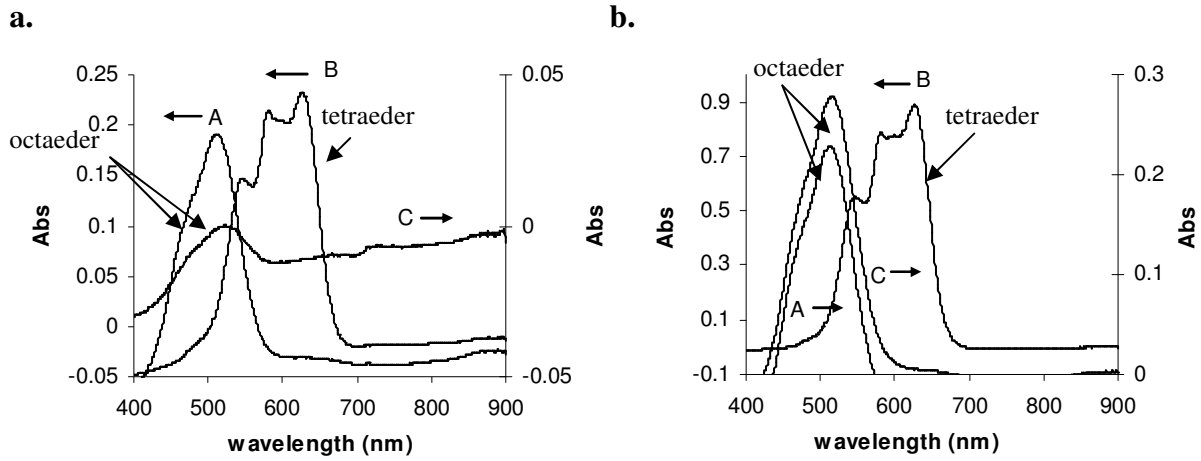


Figure 3-35. Absorption spectra of Co(II) in the aqueous phase (A) and of Co(II)-D2EHPA complex in hexane (B) and 1-decanol (C).
a. liquid-liquid extraction without acetate in aqueous phase,
b. liquid-liquid extraction in the presence of 0.25 mol.L^{-1} acetate in aqueous phase

The cobalt(II) ion, with the electron configuration d^7 may have its ground state configuration in either an octahedral or a tetrahedral ligand field (see Table 1-3). The octahedral cobalt species were present in the aqueous solution of cobalt(II) (spectrum 3-35A)

and in the Co(II)-D2EHPA complex in 1-decanol (spectrum 3-35C) while the same complex formed in hexane (spectrum 3-35B) was in a typical tetrahedral coordination [3_17, 3_21, 3_28]. A higher absorbance was reached in the presence of acetate ions in the aqueous phase due to a higher extraction percentage. The spectra were in accordance with the colours of the complexes formed. In 1-decanol, the absorption band of the Co(II)-D2EHPA complex (pink colour) was shifted to higher energies (or lower wavelength) compared with the cobalt complex in an inert diluent (blue colour).

Band intensities and positions in the absorption spectra of Figure 3-35 indicate the tetrahedral coordinated Co^{2+} ion in hexane [3_26-3_28]. A tetrahedral coordinated cobalt(II) ion should show three spin-allowed d-d transitions from the ground state, $^4A_2(F)$, to the states $^4T_2(F)$, $^4T_1(F)$ and $^4T_1(P)$ respectively [3_21]. The visible spectrum is dominated by the highest energy transition, $^4A_2(F) \rightarrow {}^4T_1(P)$ and this band is shown in Figure 3-35. The other two transitions occurred in the near-infrared region of the spectrum.

In the case of an octahedral configuration, also three spin-allowed transitions are expected from the ground state $^4T_{1g}(F)$, to the states $^4T_{2g}(F)$, $^4A_{2g}(F)$ and $^4T_{1g}(P)$, respectively [3_21]. This last transition is shown in the spectrum of Figure 3-35, which is also the highest energy transition, but the $^4A_{2g}(F)$ level is usually close to the $^4T_{1g}(P)$ level and therefore the transitions to these two levels are close together. The $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ generally occurs in the near-infrared region.

So, it can be stated that 1-decanol is able to coordinate to the central Co^{2+} ion in the complex resulting in a rearrangement of the bonding geometry compared with an inert diluent. The complex changes from blue to pink and its spectrum can be assigned to an octahedral bonding geometry instead of a tetrahedral configuration formed in hexane.

In Figure 3-36, the absorption spectrum of the cobalt(II) complex with D2EHPA (spectrum 3-36A) in hexane is compared to the spectrum obtained with LIX 860-I (spectrum 3-36B) and the mixture of D2EHPA and LIX 860-I (spectrum 3-36C) in the presence of acetate ions. Figure 3-36 shows a different coordination between the extraction of cobalt(II) with D2EHPA and its respective mixture with LIX 860-I. In fact, the complex of cobalt(II) with a mixture of D2EHPA and LIX 860-I shows an octahedral coordination geometry in contrast to D2EHPA, which shows a tetrahedral configuration in hexane.

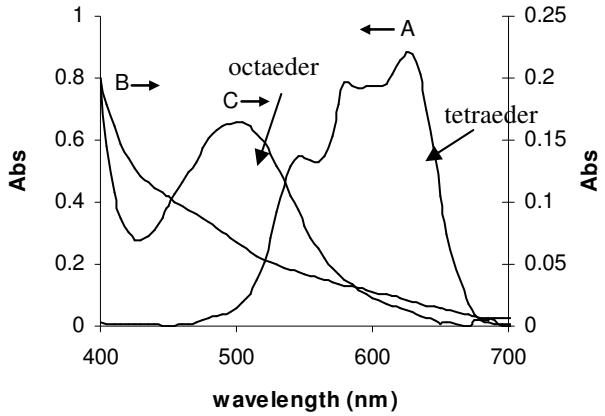
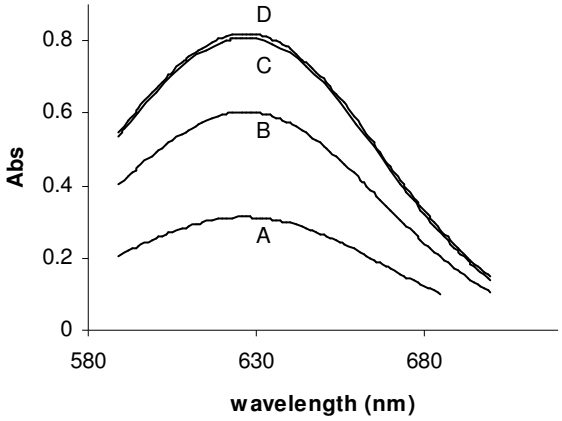


Figure 3-36. Absorption spectra of cobalt(II) complexes with D2EHPA (A), LIX 860-I (B) and its mixture (C) in hexane and in the presence of 0.25 mol.L^{-1} acetate in the aqueous phase.

3.5. CORRESPONDENCE BETWEEN THE EXTRACTION RESULTS AND ELECTRONIC ABSORPTION SPECTRA

The correspondence between the extraction results and UV-VIS absorption spectra was checked on the basis of the results obtained for nickel(II) extraction with LIX 860-I diluted in hexane and in the presence of different concentrations of acetate ions in the aqueous phase (see also Figure 3-9). The extraction percentage of nickel(II) with LIX 860-I varied in a linear way with the absorbance of the complexes obtained at 627 nm as demonstrated in Figure 3-37.

	Concentration acetate ($mol.L^{-1}$)	Absorbance	%E
A	0.05	0.312	36
B	0.10	0.608	73
C	0.25	0.808	98
D	0.50	0.819	100



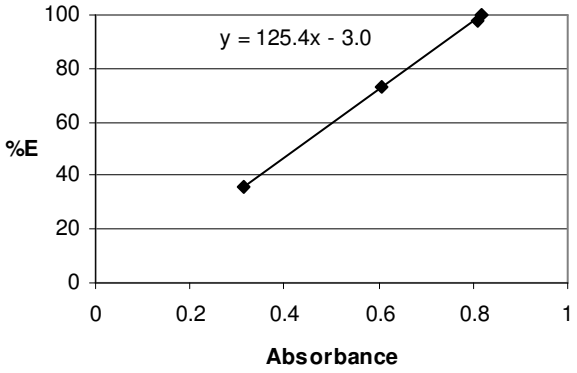


Figure 3-37. Correspondence between percentage extraction and absorbance of visible spectra

The results of Figure 3-37 show that both analyses confirm each other.

3.6. TOTAL ORGANIC CARBON ANALYSIS

The experimental program to determine whether acetate participates in the formation of the complexes was also extended with a Total Organic Carbon (TOC) analysis of the aqueous phases in the case of copper(II) and nickel(II) extraction with D2EHPA diluted in hexane. Copper(II) and nickel(II) solutions (0.0500 $mol.L^{-1}$) containing 0.25 $mol.L^{-1}$ sodium acetate were shaken with a solution of 0.250 $mol.L^{-1}$ D2EHPA dissolved in hexane. The results of the concentration differences of acetate in the aqueous phase before and after

the liquid-liquid extractions are shown in Table 3-2. In addition, a liquid-liquid extraction experiment was performed with an aqueous phase, which contained no metal ions (blanc experiment).

Table 3-2. TOC analysis of the concentrations of acetate ions in the aqueous phase

	Concentration before shaking ($mol.L^{-1}$)	Concentration after shaking ($mol.L^{-1}$)
Without metal ions	0.242	0.241
0.0500 $mol.L^{-1}$ Cu(II)	0.250	0.248
0.0500 $mol.L^{-1}$ Ni(II)	0.250	0.253

A small decline was found in the acetate concentration for the blanc and copper(II) experiment, this decline not being of any importance because of a standard deviation of 0.0017 on the measurements itself. Even a small insignificant increase was found for nickel(II).

This information confirms the previous conclusions from the infrared and UV-VIS absorption spectra that acetate and/or acetic acid do not participate in the formation of copper(II) and nickel(II) complexes.

3.7. CONCLUSION

In this Chapter, the extraction of the metal ions nickel(II), copper(II), cobalt(II), magnesium(II) and iron(III, II) with D2EHPA, LIX 860-I and CYANEX 301 was studied. Mixtures of these extractants were investigated in order to observe any synergistic behaviour. As solvents, hexane and 1-decanol were chosen in order to determine the effect of the polarity of the diluent on the extraction efficiency of the metal ions and to observe changes in the configuration of the metal complexes. FT-IR analysis and UV-VIS absorption spectra of the metal-organic phases were used to study the complexation characteristics. Furthermore, the influence of the presence of acetate ions in the aqueous phase was studied. Besides the pH-effect (Na, H) acetate may have on the extraction of metal ions, it was investigated if the aqueous phase ligands also participate in the formation of the metal-organic complexes.

Remarkable differences were found between the extraction efficiencies of an inert diluent compared to a chemically active one such as 1-decanol. With 1-decanol as diluent, the extraction percentages of copper(II), nickel(II), iron(III), cobalt(II) and magnesium(II)

decreased in the presence of LIX 860-I. LIX 860-I is able to react with a diluent with electron-donor properties, such as ethanol or 1-decanol. These interactions of the diluent with the extractant molecules affect the activity of the extractant and change the extraction performance. With the other extractant molecules, D2EHPA and CYANEX 301, extractant-diluent interactions are expected to be rather moderate. However, interactions between the diluent and the metal complex are possible. In the case of cobalt(II)-D2EHPA complexes, the diluent-metal complex interactions led to a change in coordination geometry. The UV-VIS spectra of the cobalt(II) complexes showed that in hexane a tetrahedral complex (blue color) is formed while in 1-decanol the complex has an octahedral geometry (pink color) due to the axial coordination of the molecules of 1-decanol to the central Co(II)-ion. Nickel(II) complexes usually prefer an octahedral configuration. Interaction of the diluent with the extracted nickel complex however can occur by replacement of the coordinated neutral extractant molecules and/or water molecules. However, no differences were observed in the spectrum of the Ni(II)-D2EHPA complexes. The interpretation of the spectra of the Cu(II)-D2EHPA complexes was rather difficult due to the very broad bands in the visible part of the absorption spectra. Interactions between a chemically active diluent and the copper(II) complex can occur however, resulting in a tetrahedral or octahedral configuration instead of a square-planar one in inert diluents.

If mixtures of two or more extractants are applied in the extraction process, synergistic effects are possible. One extractant complexes the metal ion and neutralizes the charge while another extractant may replace water molecules or may occupy free coordination sites. Synergism was mainly observed for the extraction of nickel(II) with a mixture of LIX 860-I and D2EHPA diluted in hexane. The extraction percentage of nickel(II) obtained with the mixture of LIX 860-I and D2EHPA was higher than the sum of the extraction percentages obtained with the independently acting extractants. The pH isotherms shifted to lower pH regions, which enables the extraction at a lower pH. The synergism between LIX 860-I and D2EHPA for the extraction of nickel(II) was not present in 1-decanol. In hexane, the spectrum of the nickel complex formed with a mixture of LIX 860-I and D2EHPA tended more towards the spectrum of LIX 860-I. In 1-decanol, the same absorption spectrum was formed as for D2EHPA separately. This can be due to the fact that in 1-decanol, already a strong interaction exists between the diluent and the metal complex, which resists any interaction with the second extractant.

The introduction of acetate ions in the aqueous phase resulted in the most profound effect on the extraction results of nickel(II), cobalt(II) and magnesium(II) with D2EHPA and

LIX 860-I. The aqueous phase additives can act as a buffering agent depending on the pH of the aqueous phase resulting in an improved extraction efficiency of the metal ions, which are only extracted at pH values above 4.5 with the applied extractants. CYANEX 301 differs from this behaviour because the pH isotherms of most metal ions are shifted to lower pH values in the presence of CYANEX 301. In general, decreasing the acidity of the aqueous phase additives by increasing the hydrophobic chain length resulted in higher extraction efficiencies. However, no evidence was found that supported an active role of acetate in the complex formation of nickel(II), copper(II) and cobalt(II). Those results were confirmed with the UV-VIS absorption spectra of the metal-organic complexes where no shifts were encountered in the presence of the aqueous phase additives. Furthermore, TOC analysis of acetate concentrations in the aqueous phases before and after the liquid-liquid extraction experiments revealed the same result.

In the case of iron(III, II) (most profound effect with LIX 860-I) and magnesium(II) (most profound effect with CYANEX 301), the acetate ions had a different effect depending on the type of diluent. In the presence of 1-decanol, improvements in extraction results were obtained due to the presence of acetate which were not observed in hexane. In the case of iron(III, II), these higher extraction results cannot be explained on the basis of the presence of a buffering agent (experiments of iron(III) and iron(II) were performed at pH 1.5 and 1.0, respectively). This indicates a correlation between the aqueous phase additives and the type of diluent used. FT-IR analysis showed that acetate (most probably acetic acid) can move from the aqueous to the organic phase in the case of 1-decanol even when no extractant is present. This means that in the case of iron (especially iron(III)) and magnesium(II), interactions between acetate/acetic acid and the corresponding metal complexes in 1-decanol cannot be excluded because of their preference towards oxygen-donor ligands.

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Chapter 4

DETERMINATION OF THE STOICHIOMETRY OF COPPER(II), NICKEL(II), COBALT(II) AND IRON(III) COMPLEXES WITH ORGANOPHOSPHOROUS ACIDS AND HYDROXYOXIME-BASED LIGANDS

Methods of metal extraction have always been a matter of interest, since they permit selective separations of trace amounts of metal ions using an appropriate complexing agent and solvent. The behaviour of metal ions in extraction systems is very dependent on the experimental circumstances as already discussed in Chapter 3. The appropriate choice of the extractant is the key factor. Other important parameters involved are the choice of the solvent and pH. In this Chapter, two methods are investigated to study the stoichiometry of the metal-organic complexes. The extractants D2EHPA, CYANEX 272, CYANEX 302, CYANEX 301 and LIX 860-I will be investigated. The study will be limited to the use of hexane as solvent and is focused on the elements of the first transition series, namely copper(II), nickel(II), cobalt(II) and iron(III). Iron(II) and magnesium(II) are not considered due to the low extraction efficiencies obtained in Chapter 3. As mentioned in Chapter 1 (Table 1-4), copper(II), nickel(II) and cobalt(II) belong to the borderline elements, whereas iron(III) can be seen as a hard acid preferring oxygen-donor ligands.

4.1. GENERAL METHODS FOR STUDYING COMPLEXES

4.1.1. Slope analysis technique

In literature, often slope analysis techniques are used to determine the stoichiometry of the metal-organic complexes [4_1-4_3]. In the case of monomeric species and assuming possible complex solvatation with neutral extractant molecules or water molecules (the complex polymerization is not taken into account), the extraction reaction and equilibrium constant can be expressed according to Equation (2-16) and (2-17), respectively.

The extraction constant can also be related to the distribution coefficient:

$$K = \frac{k_{M^{n+}} \left[H^+\right]_a^n}{\left[HL\right]_o^{m+n}} \tag{4-1}$$

where m denotes the degree of complex solvatation with neutral extractant molecules (m=0 if water molecules are responsible for the solvatation process) and:

$$\log K = \log k_{M^{n+}} - npH - (m+n)\log\left[HL\right] \tag{4-2}$$

At a constant extractant concentration and if the extractant concentrations far exceed the metal concentrations, a plot of log $k_{M^{n+}}$ against pH should give a straight line with slope n. Similarly, at $pH_{0.5}$ (pH of 50% metal extraction), $k_{M^{n+}} = 1$ and log $k_{M^{n+}} = 0$. Equation (4-2) then becomes:

$$npH_{0.5} = -(m+n)\log\left[HL\right] - \log K \tag{4-3}$$

A plot of $pH_{0.5}$ as a function of log [HL] should give a straight line with a slope of –(m+n) [4_2-4_3]. The amount of ligand molecules participating in the formation of the metal complexes is mostly deduced from these plots. However, the research results are not always unequivocal [4_1-4_3].

4.1.2. Spectrophotometric methods

Spectrophotometry is a useful tool for elucidating the composition of complex ions in solution. Spectrophotometric methods use the fact that the optical properties of solutions containing complexes usually differ from those of the constituent ions or molecules [4_4-4_5]. The change in optical behaviour is closely related to the formation of coordinate bonds. The determination can usually be rendered selective by an appropriate choice of the wavelength [4_4-4_5]. Two of the most common spectrophotometric techniques for studying complexes are [4_4- 4_5]:

1. The method of continuous variation
2. The mole-ratio method

The method of continuous variation is also known as Job's method. The principle of the method is that the mole ratio of the metal ion and ligand is varied between 0 and 1 at a constant total concentration of metal ion and ligand and the absorbance of the solutions of different composition is measured. If only one complex species has been formed, the composition of the metal complex can be calculated from the plot of the absorbances against

the mole-fraction of metal ion or ligand, as shown in Figure 4-1. In this study, the method of continuous variation is applied [4_4-4_5].

The principle of the mole-ratio method is that a series of solutions is prepared in which the concentration of one component (usually of the metal ion) is kept constant and that of the other is varied. The absorbance of the solutions is measured at a suitable wavelength and plotted versus the ratio of the variable and constant concentrations. If only one stable complex with selective light absorption is formed, the absorbance increases approximately linearly with the mole-ratio and finally reaches a constant value. With varying ligand concentration, the abscissa of the point of intersection of the two tangents gives the number of ligands in the complex (see Figure 4-1) [4_4-4_5].

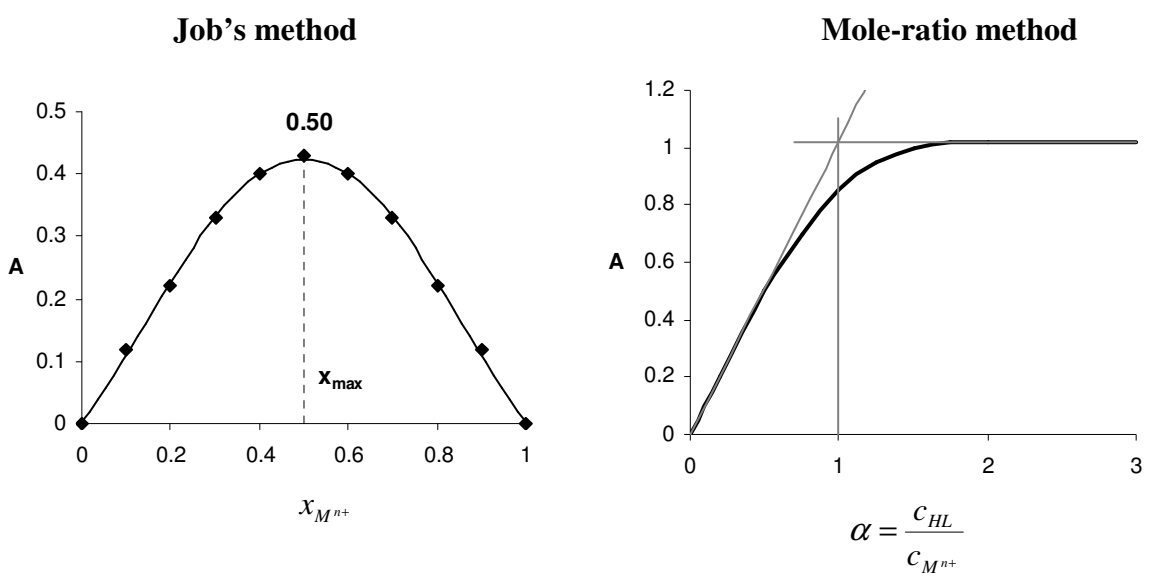

Figure 4-1. Investigation of the formation of a metal complex by spectrophotometry, using Job's method and the mole-ratio method [4_4-4_5].

In the succeeding paragraphs, a comprehensive discussion is provided on the application of Job's method for the determination of the extractant:metal ratio of the complexes of nickel(II), copper(II), cobalt(II) and iron(III) with organophosphorous acids and hydroxyoxime-based ligands. This method will be compared with the complexation behaviour of these metal ions under water-free circumstances.

4.2. DETERMINATION OF THE EXTRACTANT:METAL RATIO OF COBALT(II), NICKEL(II), COPPER(II) AND IRON(III) COMPLEXES WITH JOB'S METHOD OR METHOD OF CONTINUOUS VARIATION

4.2.1. Job's method

4.2.1.1. Monomeric extractant molecules

Assuming that monomeric extractant molecules and complex solvatation with neutral extractant molecules can occur, then the extraction reaction Equation (2-16) is valid (complex polymerization is not taken into account). The metal ion M^{n+} and monomeric extractant HL form the coloured complex $ML_n.mHL$. If water molecules are responsible for the solvatation process of the metal complex, then m=0.

The mole-ratio of the metal ion and ligand is varied between 0 and 1 at a constant total amount of monomeric ligand and metal ion. The absorption spectrum of the complex is used to determine the optimum wavelength. At this optimum wavelength, the absorption of the complex must be high, the constituents may absorb only slightly or not at all, and a small shift in the wavelength may not cause an appreciable change in the absorbance. The absorbance of solutions with varying composition is measured and plotted against the mole-fraction of the metal ion, as shown in Figure 4-1.

The mole-fraction of metal ion, $x_{M^{n+}}$, is given by the ratio of the metal ion concentration to the total concentration of metal and extractant:

$$x_{M^{n+}} = \frac{c_{M^{n+}}}{c_{M^{n+}} + c_{HL}} \tag{4-4}$$

where c_{HL} and $c_{M^{n+}}$ denote the initial analytical concentrations of respectively monomeric ligand and metal ion.

If only one complex was formed with specific composition $ML_n.mHL$, then y=m+n can be calculated from the abscissa of the maximum of the curve (x_{max}), as shown in Equation (4-4) and Figure 4-1:

$$y = \frac{1 - x_{\max}}{x_{\max}} \tag{4-5}$$

Equilibrium constants and distribution coefficients can be calculated according to Equations (2-17) and (2-14), respectively.

4.2.1.2. Dimeric extractant molecules

The extractant can also be present as dimeric molecules instead of monomeric ones [4_1-4_3]. If dimeric extractant molecules are involved in the extraction process and assuming complex solvatation with neutral extractant molecules and complex polymerization can occur, then the extraction reaction Equation (2-24) is valid. Complex polymerization is not taken into account in this work which means that p=0. If water molecules are responsible for the solvatation of the metal complex, then m=0.

For experiments using Job's method, the mole-fraction of metal ion $x_{M^{n+}}$ is now expressed as:

$$x_{M^{n+}} = \frac{c_{M^{n+}}}{c_{M^{n+}} + c_{(HL)_2}} \tag{4-6}$$

where $c_{(HL)_2}$ denotes the concentration of the dimeric ligand. It must however be noticed that only the two limits iterations are shown and that all cases lying in between them are also possible.

Extraction constants and distribution coefficients can be calculated according to Equations (2-25) and (2-14), respectively.

4.2.2. General procedure

A set of aqueous metal solutions (maximum of 10) were prepared. In a separation funnel, an appropriate amount of the aqueous phase was mixed with an appropriate amount of extractant solution in order to obtain a constant amount of metal and extractant (2.50 mmol). The metal solutions were prepared from a stock solution of 1.00 mol.L^{-1} of the appropriate chloride salt. Adding buffer to each solution (made up from its stock solution) ensured a constant pH. In the case of nickel(II) and cobalt(II), acetic acid/sodium acetate buffer (0.50 mol.L^{-1}) was used to maintain a pH of 4.8. The acetic acid/sodium acetate buffer does not influence the stoichiometry of the complex as discussed in Chapter 3. For copper(II), the pH was kept at pH 2.0 by adding phosphoric acid/sodium dihydrogen phosphate buffer (0.50 mol.L^{-1}). The pH was set at a value of 1.0 in the case of iron(III). pH adjustments were made with hydrochloric acid or sodium hydroxide. Extractant solutions were prepared from a stock solution of 0.0500 mol.L^{-1}. Hexane, purified by a fractional distillation, was used as organic diluent. The extractants D2EHPA, CYANEX 272, CYANEX 302 and CYANEX 301

were used as received. For LIX 860-I, the pure component 5-dodecylsalicylaldoxime was applied in the experimental procedure. An overview of the properties of the extractants is given in Annex A, Tables A-1 until A-3.

At room temperature, the funnels with 50.00 mL of organic phase and 50.00 mL of the aqueous metal solution were placed into a shaker over night to assure equilibrium. After settling and separation of the two phases, the absorbance of the complex was measured spectrophotometrically. The optimum wavelength was obtained from the absorption spectrum of the complex from 190 to 900 nm. The optimal wavelength was chosen in the visible part of the spectrum due to ligand interferences in the ultraviolet region. The absorbance of the organic phase was for each solution plotted against the mole-fraction of metal ion and the maximum of the plot, x_{max}, was calculated by fitting a third order expression through the experimental data. In addition, the final metal concentration in the aqueous phase was measured as well as the equilibrium pH. Through mass balance, the concentration of metal in the organic phase was calculated and plotted against $x_{M^{n+}}$ in order to confirm the results obtained with spectrophotometry. The mass balance results are only depicted if any discrepancy was found with the spectrophotometric method. At the same time, equilibrium constants and distribution coefficients were determined applying Equations (2-17) and (2-14) for monomeric ligands. The complex solvatation with neutral extractant molecules or water molecules is also taken into consideration, but no complex polymerization was assumed.

Table 4-1 shows the initial metal and extractant concentrations in the aqueous and organic phase, respectively, for the corresponding mole-fraction of metal ion. In addition, the most common extractant:metal ratios are mentioned.

Table 4-1. Initial metal and extractant concentrations of Job's method.

$x_{M^{n+}}$	metal concentration aqueous phase ($mol.L^{-1}$)	extractant concentration organic phase ($mol.L^{-1}$)	Extractant:metal ratio
0.10	0.00500	0.0450	
0.20	0.0100	0.0400	4:1
0.25	0.0125	0.0375	3:1
0.30	0.0150	0.0350	
0.33	0.0165	0.0335	2:1
0.40	0.0200	0.0300	
0.50	0.0250	0.0250	1:1
0.60	0.0300	0.0200	
0.70	0.0350	0.0150	
0.80	0.0400	0.0100	1:4

In general, the experimental procedure was used as described above, although some exceptions had to be made, especially for D2EHPA and CYANEX 272 regarding pH and extractant/metal concentrations. Higher initial pH values or higher concentrations were used to reach sufficient absorbances. In Table 4-2, an overview is given of these exceptions.

Table 4-2. Overview of the exceptions on the general experimental circumstances.

Extractant	Metal ion	pH	total amount of metal ion and ligand (mmol)
D2EHPA	Ni(II)	4.8	25.0
	Cu(II)	2.0	25.0
	Fe(III)	1.8	12.5
CYANEX 272	Cu(II)	3.0	25.0
	Fe(III)	1.8	2.50
CYANEX 302	Ni(II)	4.8	25.0

In the succeeding paragraphs, a detailed discussion will be given of the determination of the extractant:metal ratio of copper(II), nickel(II), cobalt(II) and iron(III) complexes with D2EHPA, LIX 860-I and CYANEX reagents. In addition, equilibrium constants and distribution coefficients will be calculated. Experimental data are included in Annex C, Tables C-1 until C-19.

4.2.3. Discussion of the extractant:metal ratio of copper(II), nickel(II), cobalt(II) and iron(III) complexes defined with Job's method

The results of Job's method will be presented and discussed for each extractant separately in the succeeding paragraphs.

4.2.3.1. D2EHPA

Figure 4-2 displays the results of the extraction studies of nickel(II), cobalt(II), copper (II) and iron(III) with D2EHPA. The maxima, calculated by fitting a third order expression through the experimental points, are also depicted on Figure 4-2 and are summarized in Table 4-3.

Nickel(II)

In the case of nickel(II) extraction with D2EHPA, a maximum was found at 0.32, which suggests an extractant:metal ratio of 2:1. Nickel(II) can form square-planar, tetrahedral or octahedral complexes as shown in Table 1-3. The absorption spectrum of the nickel(II)-D2EHPA complex obtained in Chapter 3 showed however the formation of octahedral species in an inert diluent such as hexane.

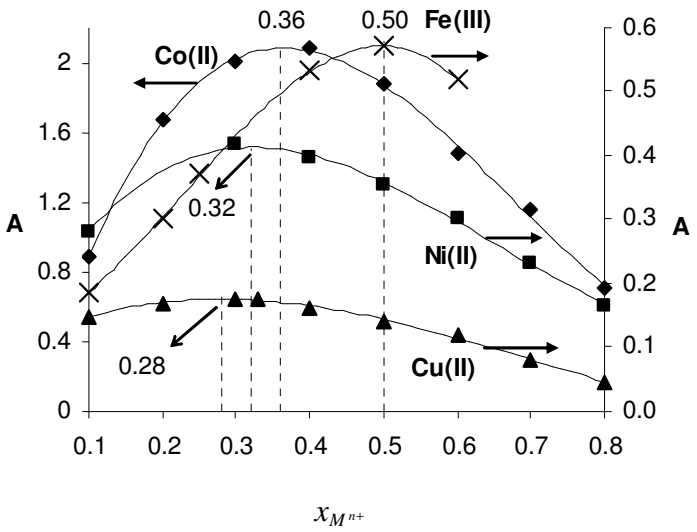

Figure 4-2. Continuous variation plot of nickel(II) [λ=401 nm], cobalt(II) [λ=626 nm], copper(II) [λ=866 nm] and iron(III) [λ=544 nm] complexes with D2EHPA.

Table 4-3. Calculated maxima of the continuous variation plots of D2EHPA

Metal ion	x_{max} (calculated)
Ni(II)	0.32
Co(II)	0.36
Cu(II)	0.28
Fe(III)	0.50

To obtain the octahedral configuration, two bidentate units of D2EHPA surround the nickel(II) ion and two water molecules must occupy the axial positions of the complex (see Figure 4-3). This means that [$ML_2.2H_2O$] nickel(II)-D2EHPA complexes are formed.

In literature [4_6], the formation of octahedral nickel(II) complexes, viz. [$(NiL_2.2H_2O)_3$], was proposed during the extraction of nickel(II) from sulfuric acid solutions with D2EHPA dissolved in hexane. Complex polymerization was however not taken into account in this study.

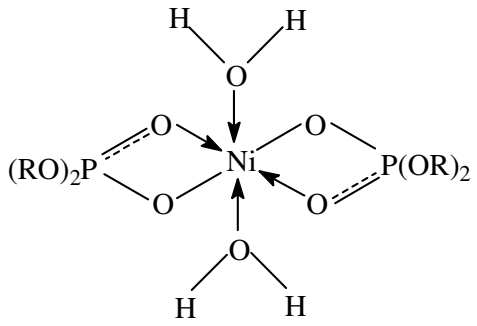

Figure 4-3. Octahedral coordination of nickel(II) with D2EHPA

Cobalt(II)

When cobalt(II) is considered, the maximum was observed at 0.36. This result deviates slightly from the value of 0.33, which would be expected in order to maintain the electrical neutrality of the membrane phase. The most common geometries of cobalt(II) complexes are tetrahedral or octahedral (see Table 1-3). The absorption spectrum of the cobalt(II)-D2EHPA complex obtained in Chapter 3 showed however the formation of tetrahedral species in hexane. The formation of [ML_2] is therefore more justified (see also Figure 4-4) [4_7].

In literature [4_6], the formation of tetrahedral [$CoL_2.2H_2O$] complexes was proposed for the extraction of cobalt(II) ions from sulfuric acid solutions with D2EHPA dissolved in hexane [4_6]. The existence of water molecules was found in the cobalt(II)-D2EHPA complex, although less strongly bound compared to the nickel(II) complex (thermal analysis) [4_6].

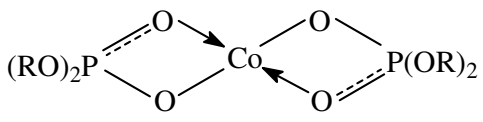

Figure 4-4. Tetrahedral cobalt(II)-D2EHPA complex

Copper(II)

In the case of copper(II), minor differences in absorbance values were obtained in the region of the mole-fraction of metal ion of 0.20 to 0.40. The calculated maximum was found at 0.28. The formation of [CuL_2] complexes seems however more justified when the absorbance value of 0.33 is considered as well as the square planar configuration, which is highly preferred by copper(II) [4_7].

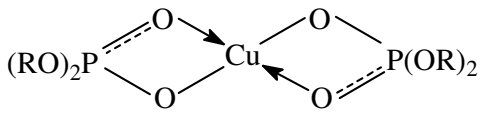

Figure 4-5. Square-planar complex of copper(II) with D2EHPA

Iron(III)

In the case of iron(III), the maximum absorbance value was found at a mole-ratio of metal ion of 0.50. This results in the formation of a 1:1 extractant:metal complex, although a contradiction is observed with reaction Equation (2-16), which expects at least an extractant:metal ratio of 3:1 in the case of trivalent iron. This implicates the co-transport of other anions into the organic phase. The chloride concentrations in the feed phase during the liquid-liquid extraction process remained however constant. These concentrations were verified by capillary electrophoresis. The lower $x_{M^{n+}}$ value can be declared by the hydrolysis

of iron(III) in the aqueous phase, which infers another extraction mechanism [4_8] which can be written as:

$$\left[Fe(OH)_2^+\right]_a + \left[HL\right]_o \leftrightarrow \left[Fe(OH)_2 L\right]_o + \left[H^+\right]_a \qquad (4\text{-}7)$$

for which an extractant:metal ratio of 1:1 is expected. Iron(III) usually prefers an octahedral configuration (see Table 1-3). This means that two water molecules must occupy the axial positions of the complex. This was also observed with nickel(II) and therefore the formation of $[Fe(OH)_2L.2H_2O]$ species is proposed.

During the past, several authors have tried already to determine the stoichiometry of the iron(III)-D2EHPA complexes, although some discrepancies may exist between the different configurations [4_8-4_10].

In a first study, 1:1 D2EHPA:iron(III) complexes were determined in the presence of 0.42 and 0.35 $mol.L^{-1}$ sulfuric acid [4_8]. In another study, the extraction of iron(III) from chloride solutions with D2EHPA was examined [4_9]. It was noticed that the compositions of the iron(III) species in both aqueous and organic phase vary with the Cl^- concentration in the aqueous phase. The formation of $[FeCl(H_2O)L_2]$ and $[FeCl_2L.(HL)_2.(HL.HCl)_2]$ at respectively 0.05 and 1.0 $mol.L^{-1}$ aqueous HCl concentrations was suggested [4_9]. A third study on the extraction of iron(III) from perchlorate media suggested that besides $[FeL_3.3HL]$, two additional complexes are formed at increasing iron(III) concentration, viz. $[Fe_3L_8ClO_4.\sim5H_2O]_n$ (n~4) and $[Fe_5L_8ClO_4(OH)_6.\ \sim7H_2O]$ [4_10]. The results of Job's method revealed a 1:1 extractant:metal ratio and is in accordance with the first study [4_10].

Summary

The results obtained with Job's method are summarized in Table 4-4 as well as the proposed configurations (monomeric ligand molecules).

Table 4-4. Overview of the proposed configurations with D2EHPA

Metal ion	x_{max} (calculated)	Complex	Configuration
Ni(II)	0.32	$ML_2.2H_2O$	octahedral
Co(II)	0.36	ML_2	tetrahedral
Cu(II)	0.28	ML_2	square-planar
Fe(III)	0.50	$M(OH)_2L.2H_2O$	octahedral

Dimeric extractant molecules

The general applied experimental procedure – explained in paragraph 4.2.2 - is principally assuming that only monomeric species are involved. This resulted in an extractant:metal ratio of 2:1 for cobalt(II), nickel(II) and copper(II), while for iron(III) an extractant:metal ratio of 1:1 was found.

In the case of D2EHPA, the extractant can however be dimeric [4_1]. In literature, the composition of the octahedral nickel(II) complex with dimeric D2EHPA molecules varied from $[Ni(HL_2)_2.(H_2O)_2]$ at low extractant concentrations to $[Ni(HL_2)_2.(H_2L_2)_2]$ at high concentrations as a result of an increase in the number of neutral $(HL)_2$ or H_2L_2 ligands bound to the nickel ion at the expense of coordinated water molecules as the extractant concentration is increased (see also paragraph 2.2.5) [4_1]. In the case of cobalt(II), application of the slope analysis technique revealed $[Co(HL_2)_2]$ complexes [4_1].

The extraction experiment of nickel(II) with D2EHPA was therefore repeated with ligand concentrations calculated in the assumption that the extractant behaves totally as a dimer. The mole-ratio of the metal ion and extractant was also varied between 0 and 1, but now at the same total amount of metal ion and dimeric ligand $(HL)_2$.

Figure 4-6 gives a comparison of the results obtained assuming only monomeric ligands are involved and for the case of totally dimeric extractant molecules. $x_{M^{n+}}$ values are expressed according to Equation (4-4) for monomeric molecules, while for dimers Equation (4-6) is used. Calculation of x_{max} indicated however the same maximum, namely $x_{M^{n+}}$ = 0.31-0.32. Spectrophotometric analysis showed in both cases the formation of octahedral complexes with two distinct maxima at 401 and 729 nm (see also paragraph 3.4.2). No shifts were found which could be related to the formation of two different complexes. In fact, at high metal loadings, the limiting ratio of D2EHPA to metal of 2:1 is approached and

extensive polymerisation of the complex can occur (see Figure 2-21) [4_1]. At higher concentrations, there can be a trend towards higher ligand participation. In our concentration range, the changes in electronic spectra were too small to identify the existence of two different complexes.

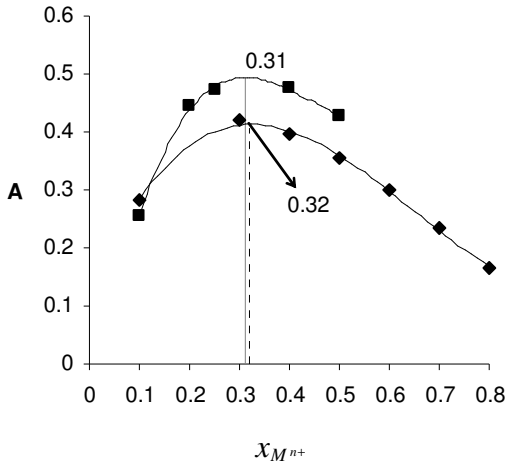

Figure 4-6. Continuous variation plot of nickel(II) [λ=401 nm] complex with D2EHPA (■ dimer; ♦ monomer).

4.2.3.2. CYANEX 272

The results of Job's method with CYANEX 272 are displayed in Figure 4-7 (see also Table 4-5). Equilibrium studies of nickel(II) are not presented due to the extremely low extraction capacity of CYANEX 272 for nickel(II) at pH 4.8. A new set of experiments was made at pH 6.0, but still not enough extraction was obtained for a distinct interpretation of the results.

Cobalt(II)

In the case of cobalt(II), the maximum of the continuous variation plot was determined at $x_{M^{n+}} = 0.32$. This corresponds to an extractant:metal ratio of 2:1. Furthermore, the absorption spectrum revealed again a tetrahedral coordination geometry, indicating that

tetrahedral complexes are formed in which cobalt(II) is surrounded by two bidentate units of CYANEX 272 [4_1, 4_3]. A similar geometry is suggested as shown in Figure 4-4.

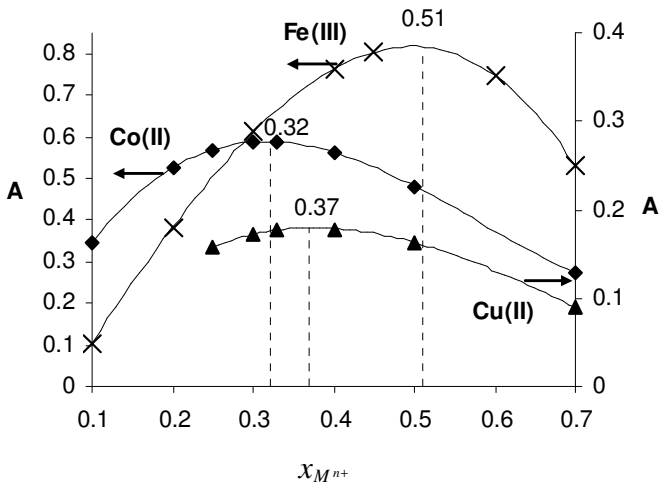

Figure 4-7. Continuous variation plot of cobalt(II) [λ=633 nm], copper(II) [λ=821 nm] and iron(III) [λ=500 nm] complexes with CYANEX 272.

Table 4-5. Calculated maxima of the continuous variation plots of CYANEX 272

Metal ion	x_{max} (calculated)
Co(II)	0.32
Cu(II)	0.37
Fe(III)	0.51

Copper(II)

When copper(II) is considered, minor changes in absorbance were again found in the mole-fraction region between 0.30 and 0.40. Calculation of the maximum of the continuous variation plot by means of the third order expression led to a maximum of 0.37. A four-coordination geometry is often preferred by copper(II) (see Table 1-3). Therefore, an extractant:metal ratio of 0.33 is more justified. The same geometry is suggested as shown in Figure 4-5.

Iron(III)

In the case of iron(III), the maximum absorbance value was found at a mole-ratio of metal ion of 0.51. This results in a 1:1 extractant:metal ratio as was also determined for D2EHPA as extractant. This is however contradictory to previous investigations on the extraction of iron(III) from aqueous nitrate solutions with CYANEX 272 [4_11]. These studies proposed the formation of [FeL_3], [FeL_3.3HL] or [$Fe(NO_3)_3$.3HL] complexes. At high HL:Fe ratio [FeL_3.3HL] is predominant, while at low HL:Fe values [FeL_3] prevails [4_11]. The extractant:metal ratio 1:1 obtained for iron(III) implicates the co-transport of other anions into the organic phase in order to maintain the electrical neutrality in the organic phase. The hydrolysis of iron(III) may also explain this behaviour (as observed with D2EHPA) and could infer the formation of [$M(OH)_2L.2H_2O$] species.

Summary

A summary of the proposed configurations is shown in Table 4-6.

Table 4-6. Overview of the proposed configurations with CYANEX 272

Metal ion	x_{max} (calculated)	Complex	Configuration
Co(II)	0.32	ML_2	tetrahedral
Cu(II)	0.37	ML_2	square-planar
Fe(III)	0.51	$M(OH)_2L.2H_2O$	octahedral

4.2.3.3. CYANEX 302

The stoichiometry of the complexes of nickel(II), cobalt(II) and iron(III) with CYANEX 302 are illustrated in Figure 4-8 (see also Table 4-7). Copper(II) results are not included. The copper complex of CYANEX 302 only allowed low absorption in the 700-900 nm wavelength range, making Job's method not applicable to determine the stoichiometric composition. Also precipitation occurred in the organic phase.

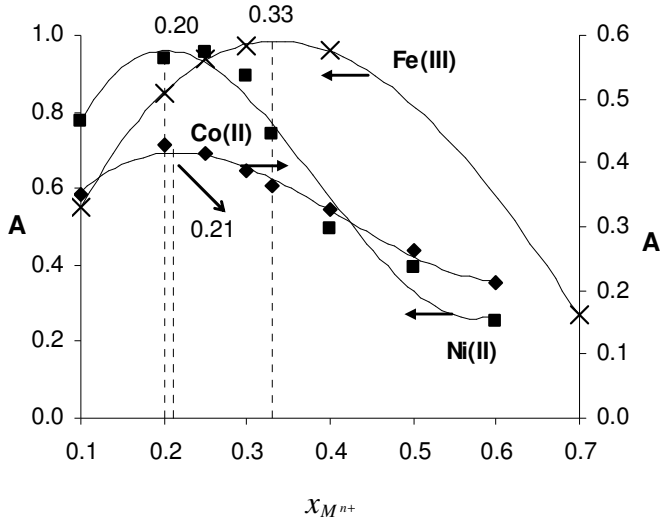

Figure 4-8. Continuous variation plot of nickel(II) [λ=681 nm], cobalt(II) [λ=730 nm] and iron(III) [λ=500 nmn] complexes with CYANEX 302.

Table 4-7. Calculated maxima of the continuous variation plots of CYANEX 302

Metal ion	x_{max} (calculated)
Ni(II)	0.20
Co(II)	0.21
Fe(III)	0.33

Nickel(II)

The maximum of the continuous variation plot of nickel(II) shifted to a lower mole-fraction of metal ion with CYANEX 302 compared to CYANEX 272 and D2EHPA, namely 0.20. This indicates the formation of 4:1 extractant:metal complexes. The replacement of coordinated water molecules by neutral ligands can explain the higher extractant:metal ratio obtained with Job's method with the bidentate ligand ($[ML_2.2H_2O]$ versus $[ML_2.2HL]$). The proposed octahedral configuration for nickel(II) in the case of monomers is shown in Figure 4-9.

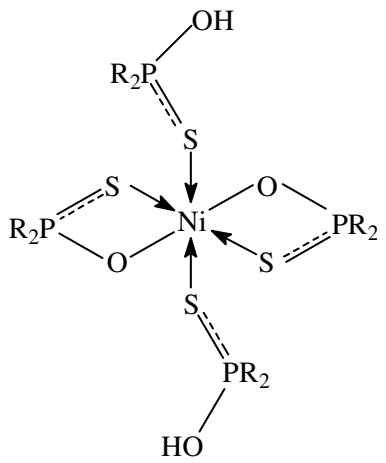

Figure 4-9. Octahedral coordination of nickel(II) with CYANEX 302 (R_2PSOH).

Cobalt(II)

The maximum of the curve of cobalt(II) also shifted to a lower mole-fraction of metal ion in the case of CYANEX 302, namely 0.21. This also indicates the formation of 4:1 extractant:metal complexes. The increase in extractant participation suggests the change of a tetrahedral configuration into an octahedral one. The same configuration for cobalt(II) is suggested as shown in Figure 4-9 for nickel(II) ($[ML_2.2HL]$).

In literature, both octahedral and tetrahedral cobalt complexes were found in hexane and xylene, although being predominantly octahedral [4_3]. Also a second study suggested an octahedral geometry [4_12]. In toluene, the existence of $[CoL_2]$ and $[CoL_2(HL)_2]$ was found, depending on the concentration of CYANEX 302 and pH [4_13].

Iron(III)

The maximum of the curve of iron(III) was determined at $x_{M^{n+}} = 0.33$. This maximum corresponds to a 2:1 extractant:metal ratio.

The replacement of one oxygen donor (CYANEX 272) by a sulfur atom (CYANEX 302) leads to a mole-fraction of metal ion of 0.33 or implicates a higher

contribution of extractant molecules in the formation of the complexes. The replacement of oxygen by sulfur enables the extraction to be carried out at a lower pH. The lower pH at which the experiments were performed, diminishes the hydrolysis of iron(III) and can possibly justify the higher extractant:metal ratio.

The experimental data did not confirm the expected extractant:metal ratio of 3:1, which was, for instance, ascertained in literature in the case of CYANEX 302 by plotting $\log k_{M^{n+}}$ against the logarithmic CYANEX 302 concentration [4_14]. In another study, the nature of some CYANEX 302 complexes was also determined by means of slope analysis techniques. A 2:1 extractant:metal complex was found for iron(III) and CYANEX 302 [4_3], as also observed with Job's method. Also the existence of both Fe(II) and Fe(III) was found in the iron solutions. Iron(III) was reduced to iron(II) and the extractant was oxidized [4_4]. This was also observed in the case of copper(II) extraction with CYANEX 302 as well as with CYANEX 301 [4_3]. The reduction of iron(III) to iron(II) and/or the lower pH at which the experiments were performed can explain the data obtained with the monothiosubstituted organophosphorous reagent [4_3].

Summary

A summary of the proposed complexes is shown in Table 4-8.

Table 4-8. Overview of the proposed configurations with CYANEX 302

Metal ion	x_{max} (calculated)	Complex	Configuration
Ni(II)	0.20	$ML_2.2HL$	octahedral
Co(II)	0.21	$ML_2.2HL$	octahedral
Fe(III)	0.33	Possible reduction of Fe(III) to Fe(II)	

4.2.3.4. CYANEX 301

Figure 4-10 displays the results of the extraction studies of nickel(II), cobalt(II), copper(II) and iron(III) with the dithiosubstituted organophosphinic acid extractant (CYANEX 301). The calculated maxima are summarized in Table 4-9.

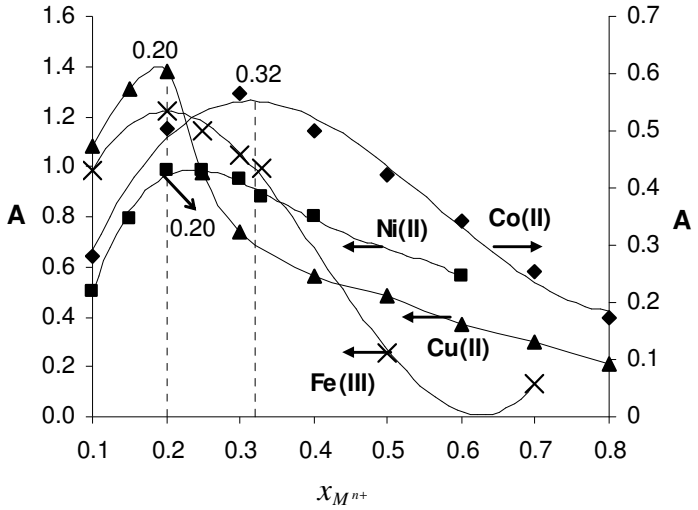

Figure 4-10. Continuous variation plot of nickel(II) [λ=563 nm], cobalt(II) [λ=674 nm], copper(II) [λ=438 nm] and iron(III) [λ=609 nm] complexes with CYANEX 301.

Table 4-9. Calculated maxima of the continuous variation plots of CYANEX 301

Metal ion	x_{max} (calculated)
Ni(II)	0.20
Co(II)	0.32
Cu(II)	0.20
Fe(III)	0.20

Nickel(II)

Nickel(II) showed its maximum at a mole-fraction of metal ion of 0.20; thus inferring an extractant:metal ratio of 4:1. In the case of nickel(II), the same extractant:metal ratio of 4:1 was found as compared to the monothiophosphinic extractant, thus inferring the same coordination pattern, viz. the formation of $[ML_2.2HL]$ species (see also Figure 4-9).

Cobalt(II)

The calculated maximum of the third order expression for cobalt(II) showed the formation of a complex with an extractant:metal ratio near to 2:1 ($x_{M^{n+}} = 0.32$). The results obtained in the case of cobalt(II) therefore suggest a tetrahedral configuration (see also Figure 4-4).

Copper(II)

As far as copper(II) is concerned, a smooth third order expression could not be fitted through the experimental results obtained, even though a distinct maximum can be seen at a mole-ratio value of metal ion of 0.20 (extractant:metal ratio of 4:1). The mass balance results of copper(II) concentrations in the aqueous phases indicated however x_{max} at 0.35 as shown in Figure 4-11.

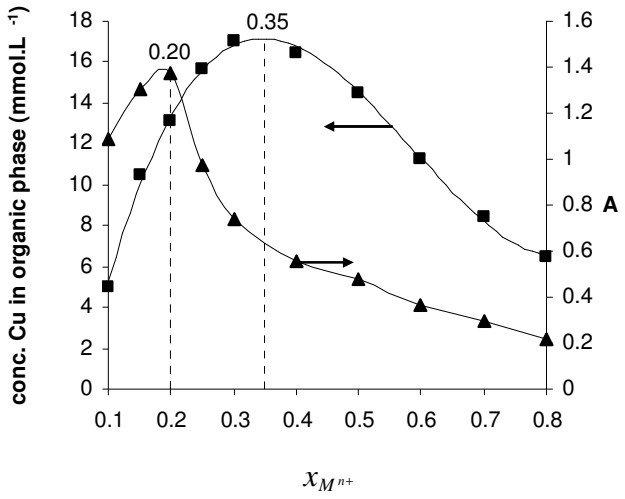

Figure 4-11. Comparison between continuous variation method based on absorbance of organic phases (▲) and on mass balance results (■) of copper(II) with CYANEX 301.

Instabilities encountered with CYANEX 301 can perhaps declare this strange behaviour [4_3]. In literature [4_3], it was mentioned that the extraction of copper(II) with CYANEX 301 can involve the reduction of the metal ion to copper(I) and the accompanying

oxidation of the ligands to the disulfide [$R_2P(S)$-S-S-$(S)PR_2$]. Acid stripping is ineffective because it is necessary to oxidize the metal ion back to the divalent state in order to obtain an effective recovery [4_3].

Iron(III)

Replacement of one oxygen donor by a sulfur atom (CYANEX 302) led to a mole-fraction of metal ion of 0.33 in the case of iron(III). A further shift towards a lower $x_{M^{n+}}$ value was seen by the replacement of the second oxygen donor by sulfur (CYANEX 301), giving an extractant:metal ratio of 4:1 at the maximum absorbance at $x_{M^{n+}}$ of 0.20.

The lower pH at which the extractions were performed by means of the thiosubstituted organophosphorous extraction reagents diminishes the hydrolysis of iron(III) - as was already mentioned for CYANEX 302 – and/or the reduction of iron(III) towards iron(II) [4_3] can justify the higher extractant:metal ratio obtained.

Summary

A summary of the proposed configurations is shown in Table 4-10.

Table 4-10. Overview of the proposed configurations with CYANEX 301

Metal ion	x_{max} (calculated)	Complex	Configuration
Ni(II)	0.20	$ML_2.2HL$	octahedral
Co(II)	0.32	ML_2	tetrahedral
Cu(II)	0.20/0.35	Possible reduction of Cu(II) to Cu(I)	
Fe(III)	0.20	Possible reduction of Fe(III) to Fe(II)	

4.2.3.5. LIX 860-I

The last type of extractant is based on the chelating oxime LIX 860-I. A sample of the pure component 5-dodecylsalicylaldoxime was applied for the liquid-liquid extraction

experiments. LIX 860-I is well-known for its chelating properties due to its hydroxyl and oxime functionality (see also paragraph 2.2.3.1). The stoichiometry of the complexes is revealed in Figure 4-12 (see also Table 4-11).

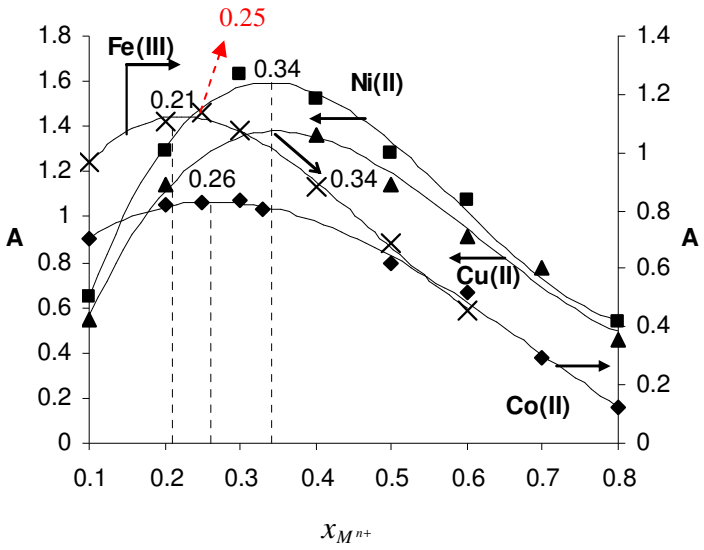

Figure 4-12. Continuous variation plot of nickel(II) [λ=627 nm], cobalt(II) [λ=600 nm], copper(II) [λ=677 nm] and iron(III) [λ=540 nm] complexes with LIX 860-I.

Table 4-11. Calculated maxima of the continuous variation plots of LIX 860-I

Metal ion	x_{max} (calculated)
Ni(II)	0.34
Co(II)	0.26
Cu(II)	0.34
Fe(III)	0.21

Nickel(II)

Nickel(II) shows the formation of a complex with stoichiometric composition [ML_2]. The calculated maximum depicted at $x_{M^{n+}}$ of 0.34 differs slightly from the value of 0.33, which is expected considering the electrical neutrality of the complex in the organic phase. In literature, investigation of the crystal structure of the bis(salicylaldoximato)nickel(II) complex

indicated the formation of a slightly distorted trans-planar geometry in the case of nickel(II) (see Figure 4-13) [4_15-4_16]. There appears to be a very strong, short, hydrogen bond between the phenolic oxygen atom and the oxime oxygen atom of the second molecule [4_16]. The results obtained with Job's method indicate the general formation of an [ML_2] complex, which can have either a square planar configuration or an octahedral configuration with two water molecules in the axial positions [$ML_2.2H_2O$] [4_15-4_16].

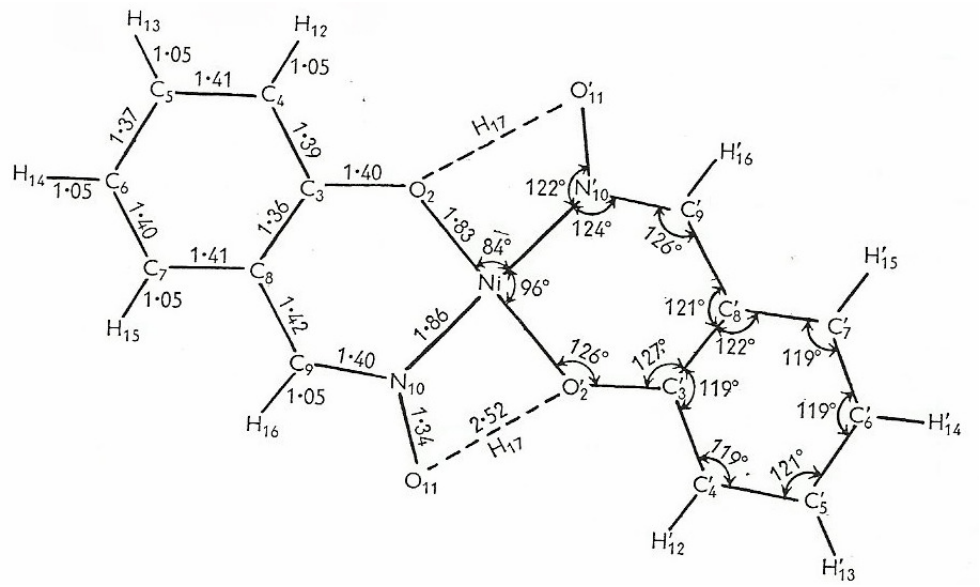

Figure 4-13. Interatomic distances and bond angles in the bis(salicylaldoximato)nickel complex [4_16].

Cobalt(II)

The determination of the stoichiometric composition of the cobalt(II) complex is less clear. The maximum absorbance revealed an [ML_3] composition, even though the absorbances only varied slightly in the mole-fraction range of metal ion between 0.20 and 0.33. This makes the prediction of the complexation behaviour rather difficult.

In literature [4_17], the oxidation of cobalt(II) to cobalt(III) was assumed when cobalt was extracted from solutions at pH 7-9, resulting in the formation of very stable cobalt(III) salicylaldoxime complexes in the solvent phase.

Bulky constituents introduced on the ligand in the third or fifth position of the aromatic ring (see Figure 4-14) were thought to favour the oxidation state of (II) for cobalt [4_17]. This is contradictory to the experimental data presented since the active component of LIX 860-I contains a dodecyl group in the fifth position of the aromatic ring, which should imply that no oxidation of cobalt(II) should occur.

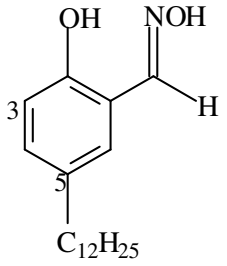

Figure 4-14. Structure of LIX 860-I

Copper(II)

Copper(II) showed the formation of a complex with stoichiometric composition [ML_2]. The extractant:metal ratio of 2:1 can be justified by a planar configuration [4_7, 4_15, 4_18]. A trans square planar coordination of two ligands around the copper(II) centre was found in literature [4_15]. A dominant feature in the structures of the free ligands and their metal complexes is the formation of hydrogen bonds between the oximic hydrogen and phenolic oxygen atoms. The formation of pseudo-macro cyclic units by such intermolecular hydrogen bonding in 2:1 complexes with copper explains the high strength and selectivity of these reagent types when used in the solvent extraction of copper (II) (see also Figure 4-15).

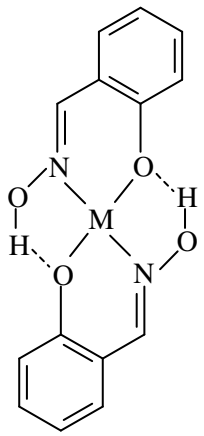

Figure 4-15. Hydrogen bonding in 2:1 complexes between phenolic oxime units and the metal ion [4_15]

Iron(III)

In the case of iron(III), the maximum of the continuous variation plot showed an $x_{M^{n+}}$ value of 0.21 (fitting of third order expression). However, the experiment with a mole-fraction of metal ion of 0.25 showed a higher absorbance. A complex with an extractant:metal ratio of 3:1 would be more justified if the electrical neutrality of the complex is taken into consideration. Little iron coordination chemistry of hydroxyoximes has been published [4_16]. Knowledge of modes of coordination of these ligands could be useful in defining the possible modes of action as corrosion inhibitors for iron, besides their excellent properties as chelating extractants. Long-chain alkyl-substituted hydroxyoximes react at mild steel surfaces to give a purple coating, which acts as a protective film against corrosion [4_16]. The simplest complex that might be proposed would be the octahedral [FeL_3], but no examples of mononuclear [ML_3] complexes have been structurally identified [4_16]. Contradictory results were obtained in another study on the complexes of iron(III) with salicylaldoxime [4_19]. The compounds contained salicylaldoxime and Fe(III) in the ratio 1:1 instead of an extractant:metal ratio of 3:1.

Summary

A summary of the proposed configurations is shown in Table 4-12.

Table 4-12. Overview of the proposed configurations with LIX 860-I

Metal ion	x_{max} (calculated)	Complex	Configuration
Ni(II)	0.34	ML_2 or $ML_2.2H_2O$	square-planar or octahedral
Co(II)	0.26	Possible oxidation of Co(II) to Co(III)	
Cu(II)	0.34	ML_2	square-planar
Fe(III)	0.21	ML_3	octahedral

4.2.4. Determination of equilibrium constants and distribution coefficients of copper(II), nickel(II), cobalt(II) and iron(III)

Job's method is a useful procedure to gain insight in the structure of the metal organic complexes. The spectrophotometric analysis of the organic phases was confirmed by the data obtained from mass balance determinations of the metal concentrations in the aqueous phase. These data also provide the necessary information to calculate the distribution coefficients of the extraction reactions. The extraction data are included in Annex C (Tables C-1 until C-19).

The distribution coefficients of nickel(II), copper(II), cobalt(II) and iron(III) are plotted in Figure 4-16 against the mole-fraction of metal ion, $x_{M^{n+}}$. 100% extraction is represented with a distribution coefficient of 100 000. In these cases, distribution coefficients could not be defined since they are extremely high. Therefore, the plots of the distribution coefficients are limited to a value of 100 000 to make a representative comparison between the extractions.

The distribution coefficients of copper(II) with D2EHPA and of nickel(II) with CYANEX 272 were too low and are not displayed in Figure 4-16. Nickel is only quantitatively extracted with the phosphinic acid type reagent at pH values above 6.

In the case of D2EHPA and CYANEX 272, the distribution coefficients were highest for iron(III). These results are consistent with the preference of iron(III) to coordinate with oxygen donor ligands [4_7].

The replacement of oxygen by sulfur increased the acidity of the extractant and favoured the extraction of copper(II), cobalt(II) and nickel(II). One drawback of the sulfur substitution is the formation of very stable complexes, which is not beneficial for the decomplexation [4_3]. It must also be noticed that stability problems limit the usefulness of the thiosubstituted organophosphinic acid extractants [4_3].

The implementation of a chelating oxime, such as 5-dodecylsalicylaldoxime or LIX 860-I, showed also good extraction properties for copper(II) and nickel(II). LIX 860-I is widely known as an excellent extractant for copper(II) recovery and has shown already its usefulness in SLM pilot installations [4_20].

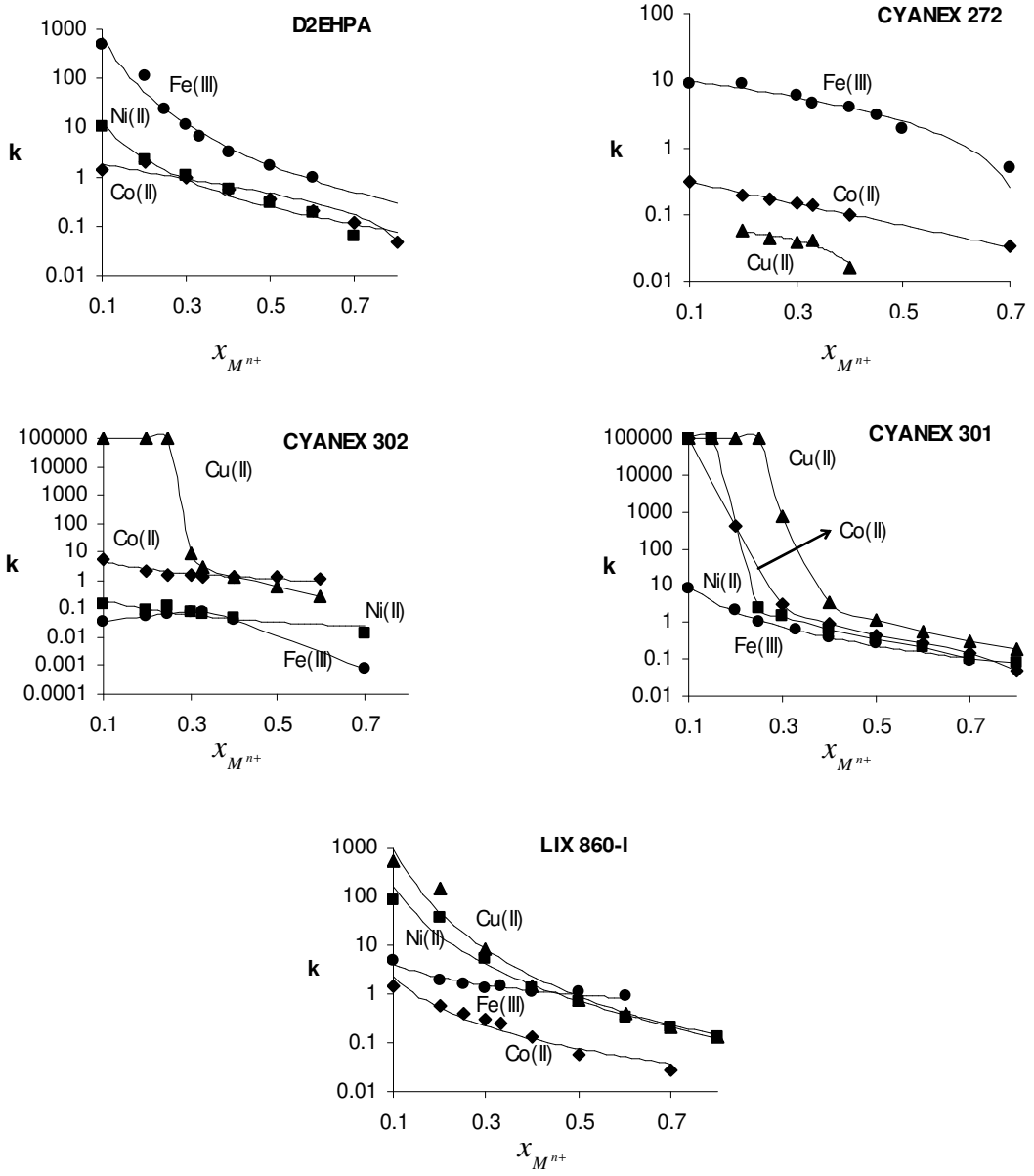

Figure 4-16. Logarithmic plot of distribution coefficient versus mole-fraction of metal ion ($x_{M^{n+}}$) for the applied extractants.

One way to express the effectiveness of the extraction system is the distribution coefficient k (and/or extraction percentage). The equilibrium constant of the extraction reaction can however also be calculated from the experimental data (see Annex C, Tables C-1 until C-19). The equilibrium constant K gives a more thorough insight in the extraction reaction because the extraction circumstances, viz. pH, and extraction mechanism are also taken into account whereas the distribution coefficient k is only dependent of the metal concentrations in both aqueous and organic phase. However, a very distinct calculation of the equilibrium constant is hardly accurate because of the low precision of pH measurement. Some doubt about the exact extraction mechanism may also interfere in the exact determination of the equilibrium constant.

In Table 4-13, an overview is given of the extractant:metal ratios defined with Job's method as well as of the equilibrium constants. These equilibrium constants are calculated on the basis of the global reaction mechanism which has been ascertained with Job's method. The equilibrium constants in Table 4-13 represent the mean value of the data of the extractions with a distribution coefficient k between 0.11 and 9. These k values correspond with extraction percentages between 10% and 90%. The metal concentrations in the aqueous phases and thus also the equilibrium constants K are more accurately detectable when the extraction percentages vary between 10% and 90%.

In the case of the copper(II)-D2EHPA, copper(II)-CYANEX 272, nickel(II)-CYANEX 302 and iron(III)-CYANEX 302 complexes, the equilibrium constant needed to be calculated on the data of the extractions with a distribution coefficient lower than 0.11, because of the low extraction results.

As expected, high equilibrium constants were generally found in the presence of CYANEX 301 and LIX 860-I. Very stable complexes can be formed with CYANEX 301, resulting however in a very difficult decomplexation [4_3].

Table 4-13. Equilibrium constants of the different extractions according to the global extraction mechanism defined with Job's method.

Extractant	Metal ion	pH	extractant:metal ratio	log K
D2EHPA	Co(II)	4.8	2:1	-5.9 ± 0.22
	Ni(II)	4.8	2:1	-5.8 ± 0.11
	Cu(II)	2.0	2:1	-3.8 ± 0.59[1]
	Fe(III)	1.8	1:1	-0.23 ± 0.16
CYANEX 272	Co(II)	4.8	2:1	-7.2 ± 0.04
	Ni(II)	4.8		
	Cu(II)	3.0	2:1	-6.4 ± 0.44[1]
	Fe(III)	1.8	1:1	0.57 ± 0.11
CYANEX 302	Co(II)	4.8	4:1	-2.4 ± 0.17
	Ni(II)	4.8	4:1	-7.0 ± 0.35[1]
	Cu(II)[2]	2.0	2:1	-5.3 ± 0.40
	Fe(III)	1.0	2:1	-0.32 ± 0.24[1]
CYANEX 301	Co(II)	4.8	2:1	-5.6 ± 0.33
	Ni(II)	4.8	4:1	1.6 ± 0.67
	Cu(II)[3]	2.0	2:1	0.92 ± 0.28
	[4]		4:1	2.3 ± 0.25
	Fe(III)	1.0	4:1	4.0 ± 0.44
LIX 860-I	Co(II)	4.8	3:1	-9.6 ± 0.16
	Ni(II)	4.8	2:1	-4.5 ± 0.42
	Cu(II)	2.0	2:1	1.2 ± 0.88
	Fe(III)	1.0	3:1	1.5 ± 0.41

[1] calculations based on data with $k < 0.11$
[2] calculations based on the assumption of an extractant:metal ratio of 2:1
[3] calculations based on results of absorbance measurements of organic phases
[4] calculations based on mass balance data of copper concentrations

4.2.5. Conclusion about the determination of the extractant:metal ratio of cobalt(II), nickel(II), copper(II) and iron(III) complexes with the method of continuous variation

The extractant:metal ratio of the different complexes has been defined by the method of continuous variation. The experiments have been carried out on the basis of monomeric extractant molecules. The results were compared with the data available from literature. These data are often based on slope analysis techniques, but are not always obtained under comparable experimental circumstances.

The results showed that D2EHPA and CYANEX 272 form similar complexes. In fact, tetrahedral, octahedral and square-planar species were formed in an inert diluent, such as hexane, for respectively cobalt(II), nickel(II) and copper(II) with D2EHPA and CYANEX 272. In each case, an extractant:metal ratio of 2:1 was found. In order to obtain the octahedral coordination in the case of nickel(II), two water molecules should occupy the axial positions (formation of $[ML_2.2H_2O]$ instead of $[ML_2]$). Iron(III) deviates from this behaviour, for which 1:1 extractant:metal complexes were found in the case of D2EHPA and CYANEX 272. Liquid-liquid extraction experiments indicated however no chloride removal (accompanying anion) from the aqueous solutions, which infers the participation of hydroxyl ions in the extraction mechanism.

The introduction of sulfur atoms in the ligands enables the metal extraction to be carried out at lower pH. In addition, the configuration of the metal complexes is influenced. In the case of the monothiophosphinic acid, an extractant:metal ratio of 4:1 was obtained for cobalt(II) and nickel(II). The higher ligand participation in the nickel(II) complex can be explained by the solvatation of the complex with neutral extractant molecules $[ML_2.2HL]$ replacing water molecules $[ML_2.2H_2O]$. In the case of cobalt(II), the higher extractant:metal ratio can be explained by the formation of octahedral species instead of tetrahedral complexes. In this case, neutral extractant molecules are responsible for the solvatation of the cobalt(II) complex. Copper(II) measurements were not included because of precipitation in the organic phase. In the case of iron(III), a higher ligand contribution was obtained with CYANEX 302 (extractant:metal ratio = 2:1). The higher ligand participation can be explained either by the lower experimental pH or by the possible instability of this reagent type.

In the presence of CYANEX 301, an extractant:metal ratio of 2:1 was ascertained in the case of cobalt(II), suggesting a tetrahedral configuration ($[ML_2]$ species). In the case of

nickel(II), the continuous variation plot depicted its maximum at a mole-fraction of metal ion of 0.20 as was also the case with the monothiophosphinic analog. The replacement of coordinated water molecules by neutral ligand molecules can justify the higher extractant:metal ratio. The determination of the configuration of the copper(II) complex with CYANEX 301 was rather difficult because some discrepancy was found between the results based on the absorbances of the organic phases (extractant:metal ratio = 2:1) and the mass balance data of copper concentrations (extractant:metal ratio = 4:1). Instabilities of CYANEX 301 can possibly explain this behaviour. In the case of iron(III), a further shift towards a lower mole-fraction of metal ion was demonstrated for CYANEX 301 (extractant:metal ratio = 4:1) compared to CYANEX 302 (extractant:metal ratio = 2:1). The higher ligand participation in the case of the thiosubstituted organophosphorous reagents can be explained either by the lower experimental pH, resulting in reduced hydrolysis of iron(III), or by the possible instability of these reagents.

In the case of the chelating oxime, LIX 860-I or 5-dodecylsalicylaldoxime, complexes with stoichiometric composition [ML_2] were found for copper(II), which can be explained by a square planar coordination. As far as nickel(II) is considered, the [ML_2] complex can have either a square planar configuration or an octahedral configuration with two water molecules occupying the axial positions [$ML_2.2H_2O$]. The determination of the cobalt(II) complex was definitely not clear. The extractant:metal ratio of 3:1 obtained in the case of cobalt(II) can be due to an oxidation process of cobalt(II) to cobalt(III). In the case of iron(III), an extractant:metal ratio of 3:1 or [ML_3] complexes were determined.

The applied experimental procedure assumed only monomer species, although D2EHPA and CYANEX 272 are sometimes depicted as dimers. Therefore, the nickel(II)-D2EHPA extraction experiment and calculations were repeated exclusively assuming the presence of dimeric units. Both plots showed however their maximum at a mole-fraction of metal ion around 0.33. The electronic spectra gave no indications of the formation of a different complex.

Furthermore, the equilibrium constants and distribution coefficients were determined for cobalt(II), copper(II), nickel(II) and iron(III), principally stating that only monomeric extractant molecules are involved. The highest equilibrium constants were found for CYANEX 301 and LIX 860-I. The replacement of oxygen by sulfur improves the extraction of metal ions such as copper(II), cobalt(II) and nickel(II). In addition, very stable complexes can be formed with CYANEX 301, however resulting in a difficult decomplexation. On the other hand, stability problems limit the usefulness of these sulfur-substituted

organophosphorous reagents. On the other hand, LIX 860-I, containing the component 5-dodecylsalicylaldoxime, is widely known as an excellent extraction agent for copper(II).

4.3. COMPLEXATION IN ANHYDROUS MEDIUM

The results with Job's method showed that additional ligands are sometimes participating in the complexation process, viz. iron(III) with D2EHPA and CYANEX 272 (see paragraph 4.2.3.1 and 4.2.3.2, respectively). No transport of the accompanying anion of the aqueous phase (Cl^-) was determined, suggesting the formation of $[Fe(OH)_2L]$ complexes. In order to prevent hydrolysis, the complexation characteristics are now investigated under water-free circumstances. During this experimental procedure, no liquid-liquid extractions were performed, but the anhydrous metal salt was added directly to the organic phase. By following up the release of hydrogen chloride during complexation, formed by the acidic proton of the extractant and the chloride anion of the metal salt, a correlation can be obtained with the number of extractant molecules in the metal complexes.

4.3.1. General procedure

The formation of the metal complexes was carried out in a three-neck round-bottom flask placed on a magnetic stirrer (see Figure 4-17). One side of the round-bottom flask was connected to a nitrogen bottle to assure a nitrogen flow. The other side of the flask was connected to a gas-washing bottle, containing a sodium hydroxide solution. A gentle stream of nitrogen gas was led over the solution, allowing the hydrogen chloride being released during complexation being absorbed into the sodium hydroxide solution. The chloride concentrations in the sodium hydroxide solutions after absorption were determined with a Waters Capillary Ion Analyser. The sum of the total concentration of metal and ligand was kept at a constant value of 0.0500 $mol.L^{-1}$. The metals were added to the organic phase as anhydrous chloride salts. Hexane, previously purified by a fractional distillation, was used as organic diluent.

Different extractant:metal ratios were reached sequentially (stepwise procedure). In another similar experiment, the total amount of extractant was added immediately and completely from the beginning of the experiment (direct procedure). The two procedures are now discussed in detail.

Stepwise procedure

During the stepwise procedure, the gas-washing bottle was first filled with a sodium hydroxide solution of 0.01 mol.L^{-1}. Furthermore, 49.00 mL hexane and 1.00 mL of an extractant solution of 1.25 mol.L^{-1} were introduced into the round-bottom flask giving an extractant concentration in the organic phase of 25.0 mmol.L^{-1}. Finally, the anhydrous metal chloride salt (1.25 mmol) was added to the stirred solution ($c_{HL} : c_{M^{n+}}$=1:1). From that moment, nitrogen gas was led over the solution. The nitrogen flow was regulated at 100 mL.min^{-1}. The content of the gas-washing bottle was periodically poured out quantitatively into a volumetric flask and the chloride concentration of those solutions was determined with Capillary Electrophoresis. Each time, a fresh sodium hydroxide solution was brought into the gas-washing bottle.

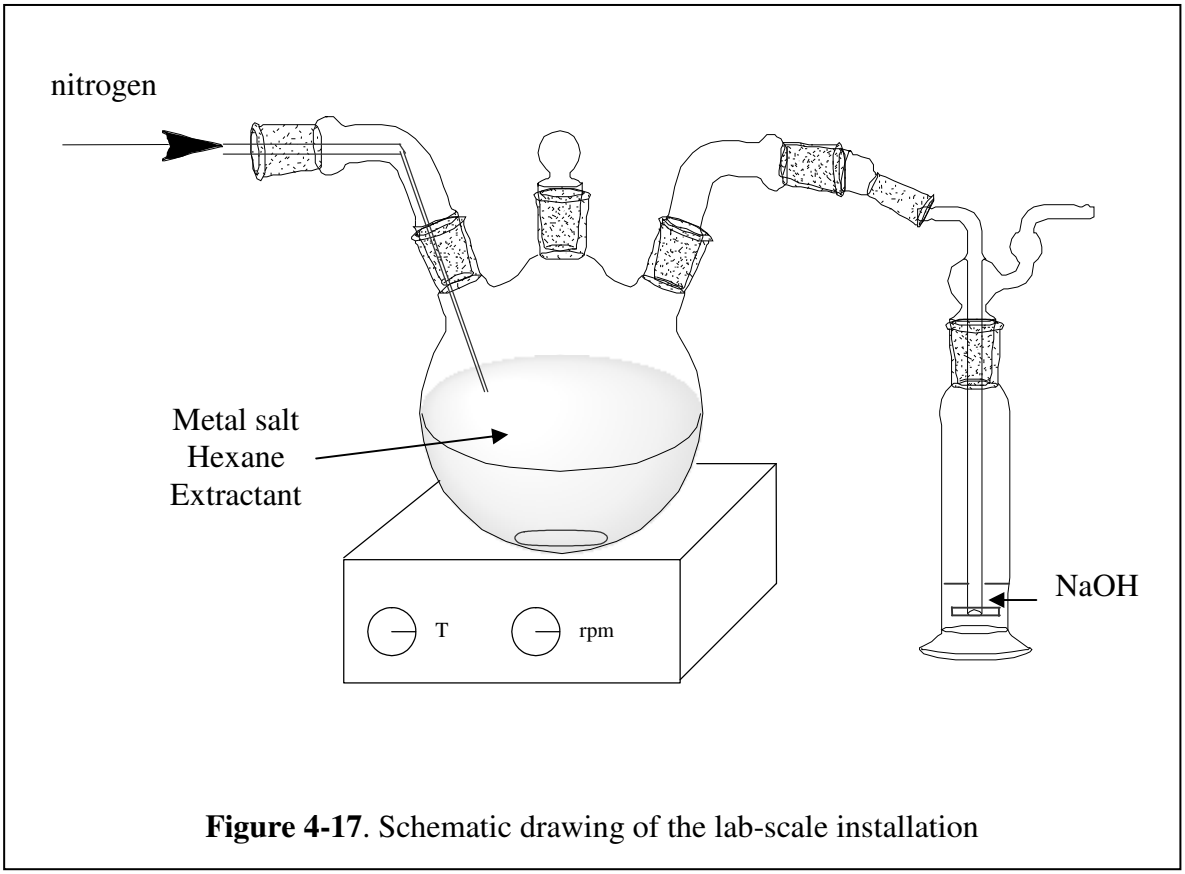

Figure 4-17. Schematic drawing of the lab-scale installation

After 23 hours, an extractant:metal concentration ratio of 2:1 was obtained through the addition of extractant (1.00 mL) and hexane (24.00 mL) to the round-bottom flask containing the anhydrous metal salt (first extra addition of ligand). This was repeated until an

extractant:metal concentration ratio of 3:1 (second extra addition of ligand after 46 hours) was reached. In the case of iron(III), the experimental procedures were stopped at an extractant:metal concentration ratio of 3:1. In the case of the divalent metal ions, a third extra addition of ligand was done after 69 hours (extractant:metal concentration ratio of 4:1) in order to have a sufficient amount of ligand in the reaction mixture. The corresponding metal and extractant concentrations during the different parts of the stepwise procedure are shown in Table 4-14. For each step, the cumulative formation of hydrogen chloride was followed for 23 hours.

Direct procedure

This stepwise procedure was also compared with another experiment containing an extractant:metal concentration ratio in the organic phase of 3:1 (iron(III)) or 4:1 (divalent metal ions) at the start of the experiment, called the direct procedure.

Table 4-14. Corresponding metal and extractant concentrations of the stepwise procedure

Step	$c_{HL} : c_{M^{n+}}$	$c_{M^{n+}}$ (mmol.L^{-1})	c_{HL} (mmol.L^{-1})
1	1:1	25.0	25.0
2	2:1	16.7	33.0
3	3:1	12.5	37.5
4	4:1	10.0	40.0

4.3.2. Release of hydrogen chloride during complexation of copper(II), nickel(II), cobalt(II) and iron(III) with D2EHPA, LIX 860-I and CYANEX reagents in anhydrous media

In the succeeding paragraphs, the results of the experimental procedure under water-free circumstances will be presented and will be discussed for each extractant separately (see also Annex D, Tables D-1 till D-18). For iron(III) and copper(II), a stepwise as well as a direct procedure were made. For nickel(II) and cobalt(II), only experiments with the direct procedure were performed to gain a first insight in its complexation characteristics in anhydrous media. In addition, FT-IR spectra as well as UV-VIS absorption spectra of the hexane phases were recorded. Only the most profound changes are shown in this work.

4.3.2.1. D2EHPA

The amount of hydrogen chloride released during the complexation of iron(III), copper(II), nickel(II) and cobalt(II) with D2EHPA is given in Figure 4-18.

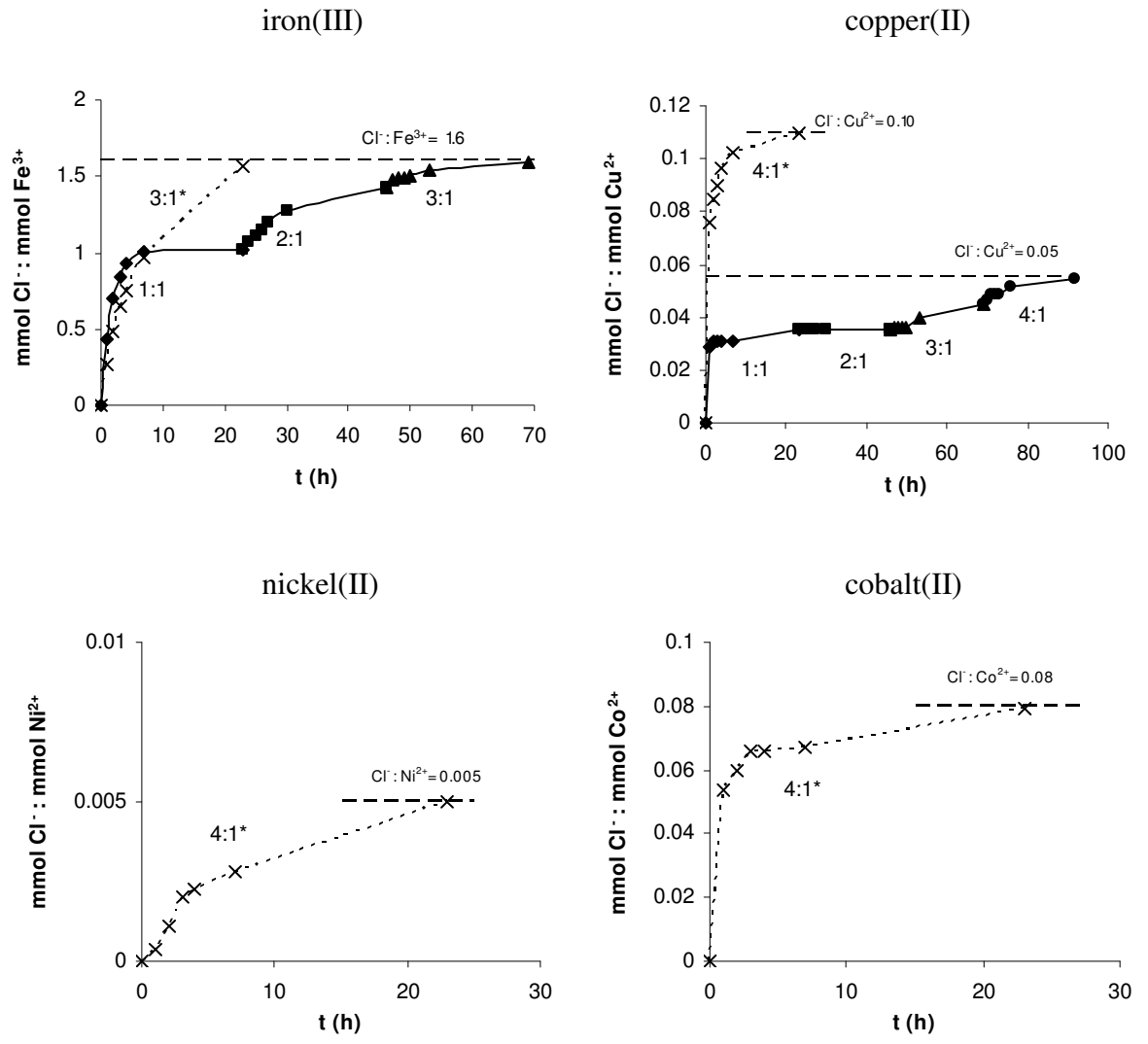

Figure 4-18. Release of chloride ions as a function of time during complexation of $FeCl_3$, $CuCl_2$, $NiCl_2$ or $CoCl_2$ with D2EHPA in anhydrous media.

The amount of hydrogen chloride released during complexation is depicted as the ratio of the cumulative amount of Cl^- ions measured in the sodium hydroxide solution (mmol) to the total amount of metal (1.25 mmol) present in the round-bottom flask as a function of time.

The data of iron(III) and copper(II) show two processes, viz. the stepwise and direct procedure. The direct procedure is labelled as "*".

Iron(III)

In the case of iron(III), the amount of chloride ions in the receiving phase gradually increased. During the first addition of extractant, theoretically 1.25 mmol HCl can be formed, which corresponds to an extractant:metal ratio of 1:1. This maximum value or Cl^-:Fe^{3+} ratio of 1 is reached quite fast. During the second step, more hydrogen chloride is formed, but the kinetics are slower compared to the first addition of extractant. This is also the case during step 3. Finally, a Cl^-:Fe^{3+} ratio of 1.6 is reached after 69 hours. Approximately the same value was obtained when repeating the experiment with the addition at one time of the total amount of D2EHPA (direct procedure). Thus, in the case of the complexation of iron(III) with D2EHPA, it is clear that the extractant:metal ratio of 3:1 - which accounts for 3.75 mmol Cl^- - is not reached, at least not after 69 hours. This behaviour is quite similar to the data obtained with Job's method. The complexation of one extractant molecule proceeds quite easily and involves the presence of two chloride ions in the iron complex because of the absence of water molecules. The further exchange of a chloride ion by a second D2EHPA molecule is also proven in Figure 4-18, although the reaction process is slower compared to the first step of the process. A similar trend is found during the last addition of extractant. This supports the idea that an extractant:metal ratio of 3:1 is not a necessary condition for iron(III) extraction with D2EHPA. Even the coexistence of $[FeCl_2L]$, $[FeClL_2]$ and to a smaller extent $[FeL_3]$ is quite presumable.

A new direct procedure experiment was done with D2EHPA and iron(III) to check the influence of water on the complexation behaviour. A total of 1.66 mmol HCl was absorbed by the sodium hydroxide solution. At the end of this new experiment, the hexane phase was collected into four fractions of 25 mL. Each fraction was shaken one hour with 25 mL pure water or with slightly acidified water. For acidification, sulfuric acid was added to the water until pH 1.0 and 1.8 or nitric acid was added until pH 1.8 was reached. The amount of chloride ions as well as iron(III) released into the aqueous phase were determined respectively by titration with silver nitrate and Atomic Absorption spectroscopy. The amount of chloride ions and iron(III), collected in each fraction, are represented in Table 4-15.

The results show that the chloride ions of the iron(III) complexes in the organic phase are easily exchanged and replaced by hydroxyl groups. Even the type of aqueous phase has no influence on the data. Calculation of the mass balance of Cl^- showed a recovery of 95%. A loss of 5% may be justified by the various experimental steps in the procedure. At the same time, the stripped amount of iron(III) is nearly negligible, except in the case of sulfuric acid at pH 1.0. Furthermore, the sulfate and nitrate concentrations in the aqueous phase at pH 1.8 – determined with capillary electrophoresis – remained constant during shaking.

Table 4-15. Replacement of chloride ions from the anhydrous iron(III)-D2EHPA complex of the direct procedure by hydroxyl groups.

aqueous phase	initial pH	pH after scrubbing	Cl^- (mmol)	Fe (mmol)
H_2SO_4	1.0	/	0.48	0.10
	1.8	/	0.49	0.01
HNO_3	1.8	1.5	0.49	0.01
H_2O	5.9	2.0	0.44*	0.001

* The lower Cl^- value in the presence of water is due to the lower remaining fraction of hexane phase – 22.5 mL - that could be treated with water (due to evaporation)

In addition, the pH of the aqueous phases after scrubbing (nitric acid scrub and water) was checked as a further evidence of the Cl^--OH^- exchange. The pH decreased towards 1.5 for the nitric acid scrub and towards 2.0 for the not acidified water. These experiments obviously prove a preferred coordination of iron(III) with hydroxyl groups instead of chloride, sulfate or nitrate anions, as already observed during Job's method.

Copper(II)

In the case of copper(II), only limited complexation was observed. D2EHPA preferentially coordinates with iron(III) [4_7]. However, a gradual increase was observed in the case of the stepwise procedure.

Nickel(II) and cobalt(II)

In the case of nickel(II) and cobalt(II), only limited complexation was achieved compared to iron(III) (see Figure 4-18).

UV-VIS absorption spectra

Additional UV-VIS absorption spectra were recorded of the hexane phases. Only the spectra of the iron(III)-D2EHPA complexes are displayed due to the poor release of hydrogen chloride in the case of the other metal ions. Figure 4-19 shows the UV-VIS absorption spectra of the iron(III)-D2EHPA complexes of the stepwise procedure in the wavelength range of 350 to 450 nm. A broad band is formed around 358 nm, due to the yellow coloured iron(III)-D2EHPA complex. The absorption band slightly shifts towards a lower wavelength in the presence of a higher concentration of extractant, but also a decline in absorbance is observed. During the first part of the stepwise procedure, mainly [$FeCl_2L$] is formed. The limited evolution towards 2:1 and 3:1 D2EHPA-iron(III) complexes concluded on the basis of the chloride analysis results in a rather small shift of the maximum of the absorption band. The dilution during the second and third step of the process therefore prevails.

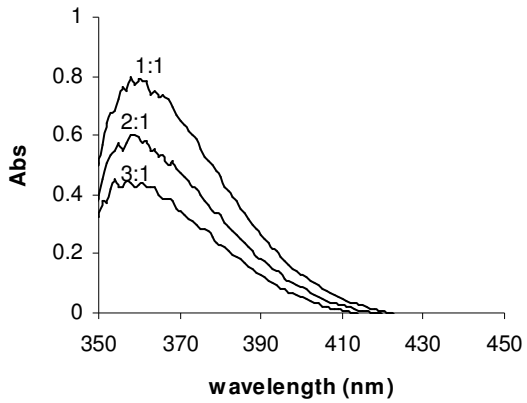

Figure 4-19. Absorption spectra of the iron(III) complexes during the stepwise procedure with D2EHPA.

FT-IR spectra

The discussion of the FT-IR spectra is limited to the discussion of iron(III) because of the limited release of hydrogen chloride in the case of copper(II), nickel(II) and cobalt(II).

The FT-IR spectra of D2EHPA and the iron(III)-D2EHPA complex (3:1 extractant:metal ratio of stepwise procedure) – in the range of 1750 to 1500 cm^{-1} - are depicted in Figure 4-20. It was rather difficult to distinguish any differences between the infrared spectra of the different extractant:metal ratios of the stepwise procedure. Therefore, only the spectrum of the last part of the stepwise procedure is displayed.

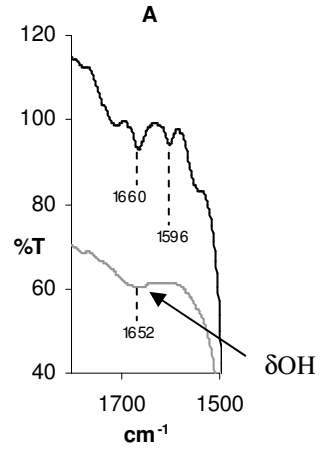

Figure 4-20. FT-IR spectra of D2EHPA (grey) and Fe(III)-D2EHPA complex (**black**).

The broad band at 1652 cm^{-1} (Figure 4-20) can be assigned to the OH deformation vibration of the organophosphoric acid [4_21]. The structure of D2EHPA is shown in Figure 4-21. In the spectrum of the complex, two sharp bands appear at respectively 1660 and 1596 cm^{-1}, instead of the broad band at 1652 cm^{-1}.

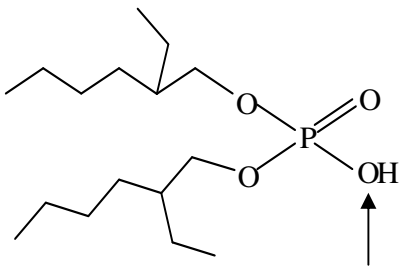

Figure 4-21. Structure of D2EHPA

4.3.2.2. CYANEX 272

In Figure 4-22, the release of hydrogen chloride during complexation of $FeCl_3$ or $CuCl_2$ with CYANEX 272 is displayed. Nickel(II) and cobalt(II) data were not registrated.

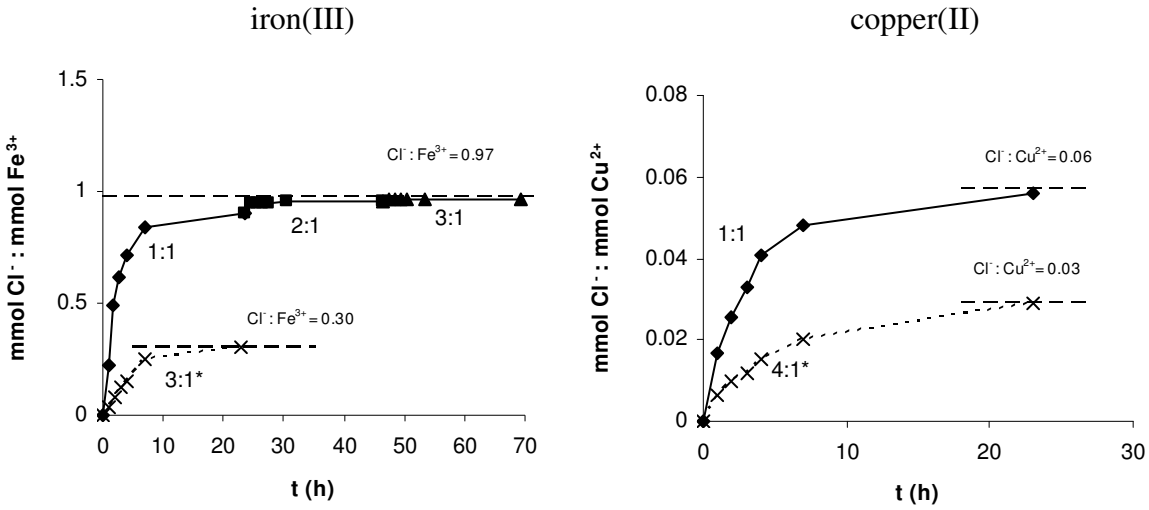

Figure 4-22. Release of chloride ions as a function of time during complexation of $FeCl_3$ or $CuCl_2$ with CYANEX 272 in anhydrous media.

Iron(III)

When using CYANEX 272, a Cl^-:Fe^{3+} ratio of 0.97 was reached during the stepwise procedure. During the first step, a Cl^-:Fe^{3+} ratio of 0.90 was found, while during the second and third step, only limited supplementary reaction was observed. These results show that the anhydrous iron salt released less chloride ions in the presence of CYANEX 272 compared to D2EHPA and corresponds to the lower extraction performance of CYANEX 272 for iron(III).

A remarkable lower result was found in the case of the direct experimental procedure of iron(III) with CYANEX 272. A Cl^-:M^{n+} ratio of 0.30 was achieved for iron(III) with the direct experimental procedure instead of a Cl^-:M^{n+} ratio of 0.97 at the end of the stepwise procedure. The lower value for the direct procedure is somewhat contradictory to the excess of extractant present in the reaction mixture. The ease of release of hydrogen chloride may however be affected by the type of extraction reagent. The presence of an oxygen-rich extractant in the reaction mixture may improve the release of hydrogen chloride (D2EHPA versus CYANEX 272).

Copper(II)

In the case of copper(II), only limited complexation was achieved with CYANEX 272 as was also the case with D2EHPA. A Cl^-:Cu^{2+} ratio of only 0.06 was found after the first part of the stepwise procedure. Also a lower result was obtained with the direct procedure (a Cl^-:M^{n+} ratio of 0.03 was reached). The direct procedure showed a lower Cl^-:Cu^{2+} ratio compared to the stepwise procedure as was also noticed for iron(III).

UV-VIS absorption and FT-IR spectra

The spectra of CYANEX 272 are not displayed in this work because of their major similarities with D2EHPA.

4.3.2.3. CYANEX 302

The results of the complexation behaviour of iron(III), copper(II), nickel(II) and cobalt(II) with CYANEX 302 are displayed in Figure 4-23. However, during the progress of the experimental work with CYANEX 302, a yellow precipitate was formed in the hexane phase, most likely sulfur. Instability problems of the complexes limit the usefulness of this extraction reagent [4_3].

Iron(III)

As far as iron(III) is concerned, a Cl^-:Fe^{3+} ratio of 0.90 was found when completing the stepwise procedure. The reaction started rather fastly during the first addition of extractant, whereas during the higher extractant:metal concentration ratios of 2:1 and 3:1, the curve nearly flattened.

It must also be noticed that a considerably smaller amount of hydrogen chloride evolved during the direct procedure with CYANEX 302 (Cl^-:Fe^{3+} = 0.62). Even a longer reaction time will not result in a higher chloride amount. A lower Cl^-:M^{n+} ratio for the direct procedure was also found with CYANEX 272, although the ratio difference between the stepwise and direct procedures is remarkably smaller in the case of CYANEX 302. The difference in extraction mechanisms involved in the formation of the metal-organic complexes, viz. higher ligand participation with CYANEX 302 compared to CYANEX 272 as

was ascertained with Job's method, and/or differences in possible interactions between free extractant or metal complexes and hydrogen chloride may affect the ease of release of hydrogen chloride.

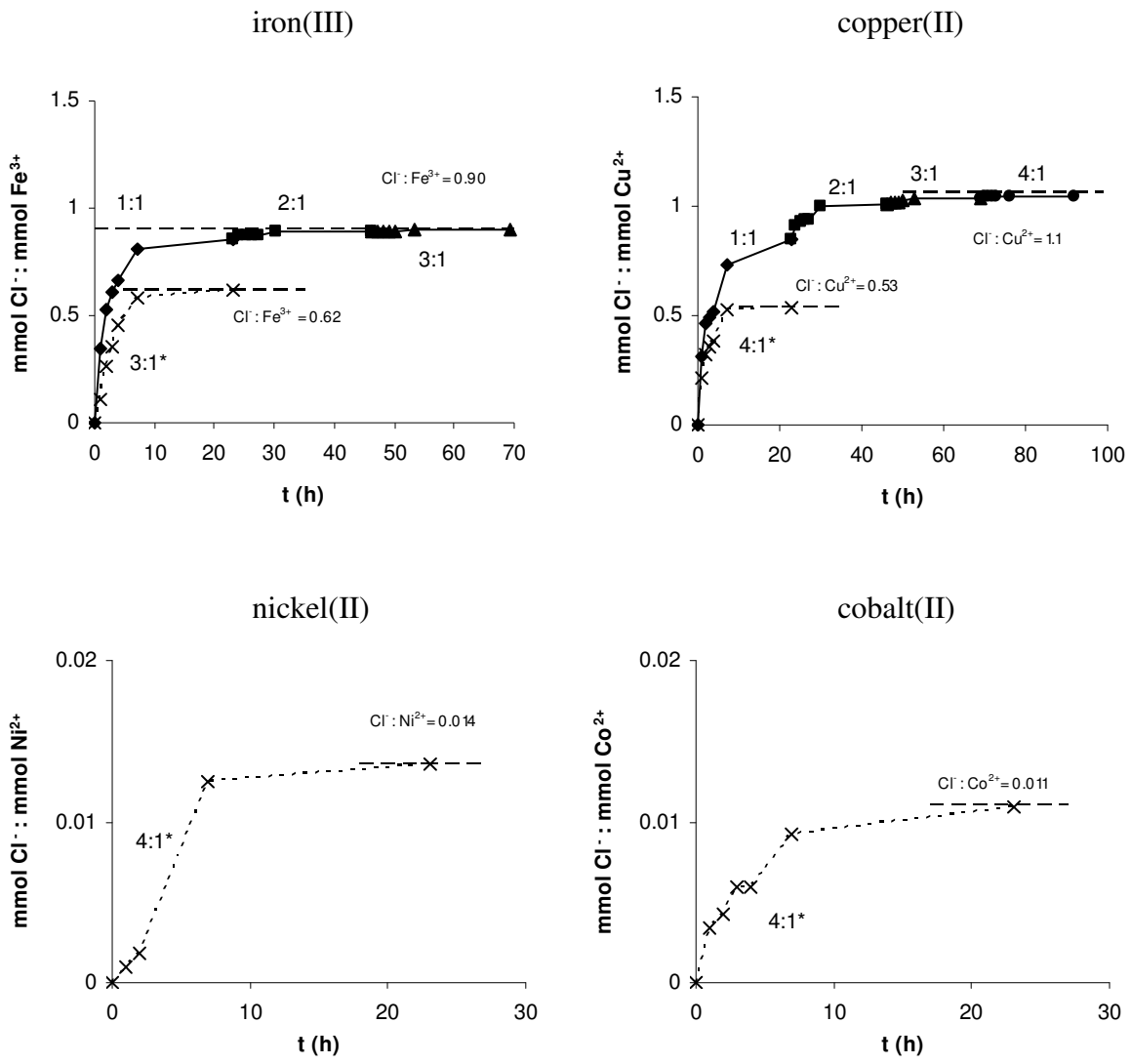

Figure 4-23. Release of chloride ions as a function of time during complexation of $FeCl_3$, $CuCl_2$, $NiCl_2$ or $CoCl_2$ with CYANEX 302 in anhydrous media.

Copper(II)

In the case of copper(II), the release of hydrogen chloride improved as compared to the complexation performance of CYANEX 272 and D2EHPA. A Cl^-:Cu^{2+} ratio of 1.1 was obtained at the end of the stepwise procedure. Again, a smaller amount of hydrogen chloride evolved during the direct procedure with CYANEX 302 (Cl^-:Cu^{2+} = 0.53).

Nickel(II) and cobalt(II)

As far as nickel(II) and cobalt(II) are concerned, only the direct procedures were again utilized to gain a first insight in its complexation behaviour with CYANEX 302. In both cases, a very poor evolution of hydrogen chloride was achieved. A Cl^-:M^{n+} ratio of 0.01 was reached for both metal ions.

UV-VIS absorption and FT-IR spectra

The UV-VIS absorption and FT-IR spectra of CYANEX 302 are not included due to the formation of a yellow precipitate, most likely sulfur. Instability problems of the complexes limit the usefulness of this extraction reagent [4_3].

4.3.2.4. CYANEX 301

The results of the release of hydrogen chloride during complexation of iron(III), copper(II), nickel(II) and cobalt(II) with CYANEX 301 are shown in Figure 4-24. Also with CYANEX 301, a yellow precipitate was formed in the hexane phase during the progress of the experimental work. Instability problems limit the usefulness of the sulfur-substituted organophosphorous reagents [4_3].

Iron(III)

In the presence of the dithiosubstituted organophosphinic acid (CYANEX 301), the Cl^-:Fe^{3+} ratio also gradually increased. During the second addition of extractant, a further release of chloride ions was observed, this in contrast to the other CYANEX reagents already discussed. The release of chloride ions during the second addition of extractant was only

minimal with CYANEX 272 and 302. Finally, a Cl^-:Fe^{3+} ratio of 1.3 was obtained during the stepwise procedure with CYANEX 301 and a slightly higher value was observed during the direct procedure. This implies that not only a Cl^-:Fe^{3+} ratio of 1 is reached, but that a higher number of extractant molecules are participating in the complex.

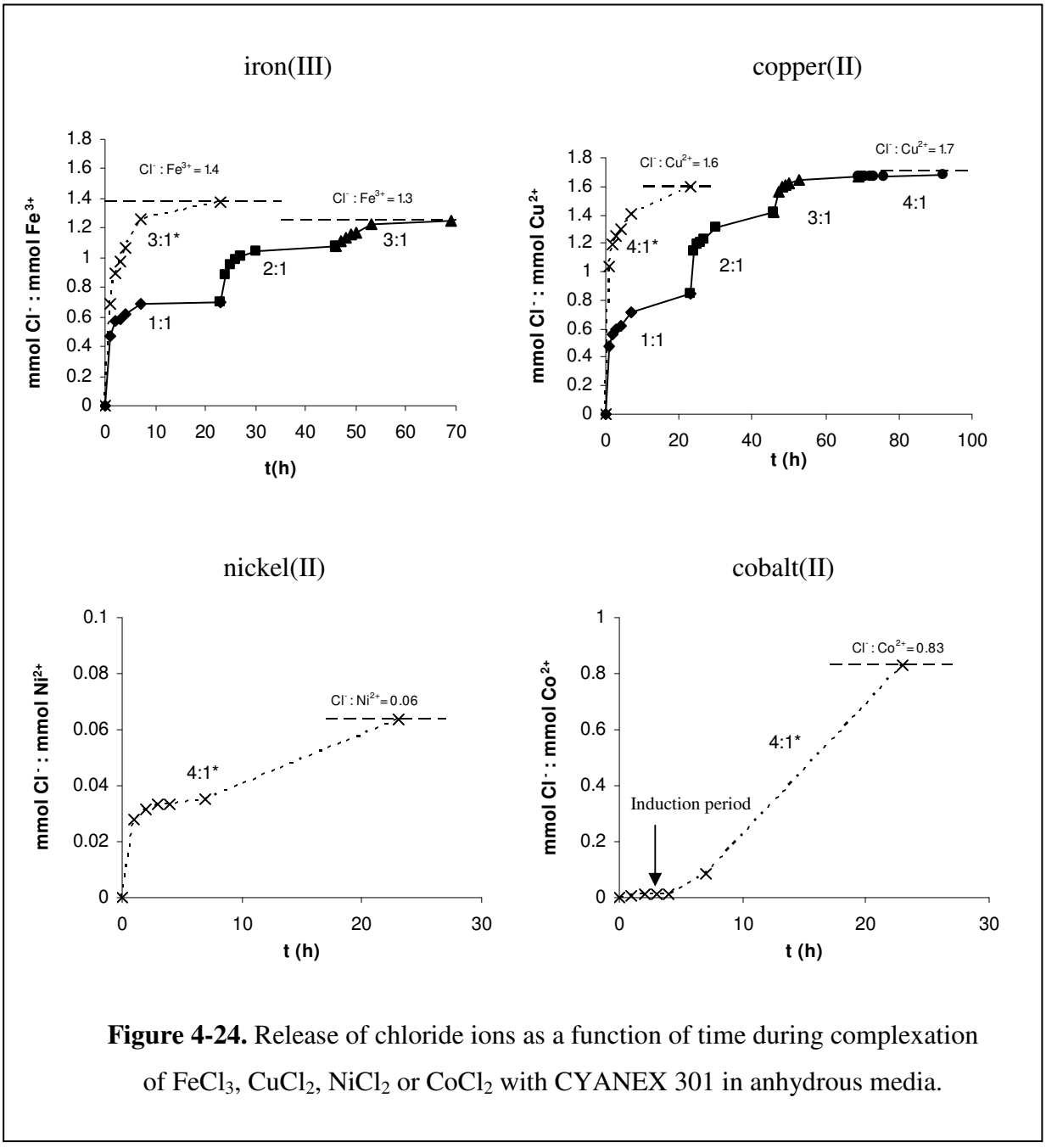

Figure 4-24. Release of chloride ions as a function of time during complexation of $FeCl_3$, $CuCl_2$, $NiCl_2$ or $CoCl_2$ with CYANEX 301 in anhydrous media.

In contrast to CYANEX 272 and 302, the $Cl^-:M^{n+}$ ratios obtained with the direct procedures are now higher than with the stepwise procedures. The difference in extraction mechanisms involved in the formation of the metal-organic complexes, viz. higher ligand participation with CYANEX 301 compared to CYANEX 302 and 272 as was ascertained with Job's method, and/or differences in possible interactions between free extractant or metal complexes and hydrogen chloride may affect the ease of release of hydrogen chloride.

Copper(II)

The complexation of copper(II) with CYANEX 301 showed the same tendency as compared to iron(III). Even a higher release of hydrogen chloride was found for both procedures ($Cl^-:Cu^{2+}$ = 1.7 and 1.6 for stepwise and direct procedure, respectively), which also shows the involvement of a higher number of extractant molecules in the copper(II) complex. In contrast to CYANEX 272 and 302, the $Cl^-:M^{n+}$ ratios obtained with the direct procedures are also higher than with the stepwise procedures.

Nickel(II) and cobalt(II)

For nickel(II) and cobalt(II), only the direct procedure was applied. Nickel(II) showed only a limited release of hydrogen chloride towards the receiving solution. In the case of cobalt(II), a $Cl^-:Co^{2+}$ ratio of 0.83 was observed, which is the highest result obtained for cobalt(II) of all extraction reagents already discussed. It is also important to note that the curvature of the graphs depicted in Figure 4-24 of nickel(II) and cobalt(II) show a somewhat different behaviour compared to iron(III) and copper(II). The curves infer that a longer reaction time can have a major influence on the final $Cl^-:M^{2+}$ ratio. Furthermore, in the case of cobalt(II), it seems that there exists an induction period.

UV-VIS absorption and FT-IR spectra

The UV-VIS absorption and FT-IR spectra of CYANEX 301 are also not included due to colour changes of the hexane phase and the formation of a yellow precipitate, most likely sulfur. Instability problems limit the usefulness of the sulfur-substituted organophosphorous reagents [4_3].

4.3.2.5. LIX 860-I

The same experiments were also performed with a hydroxyoxime-based extractant, viz. 5-dodecylsalicylaldoxime or the pure component of LIX 860-I. The results are shown in Figure 4-25.

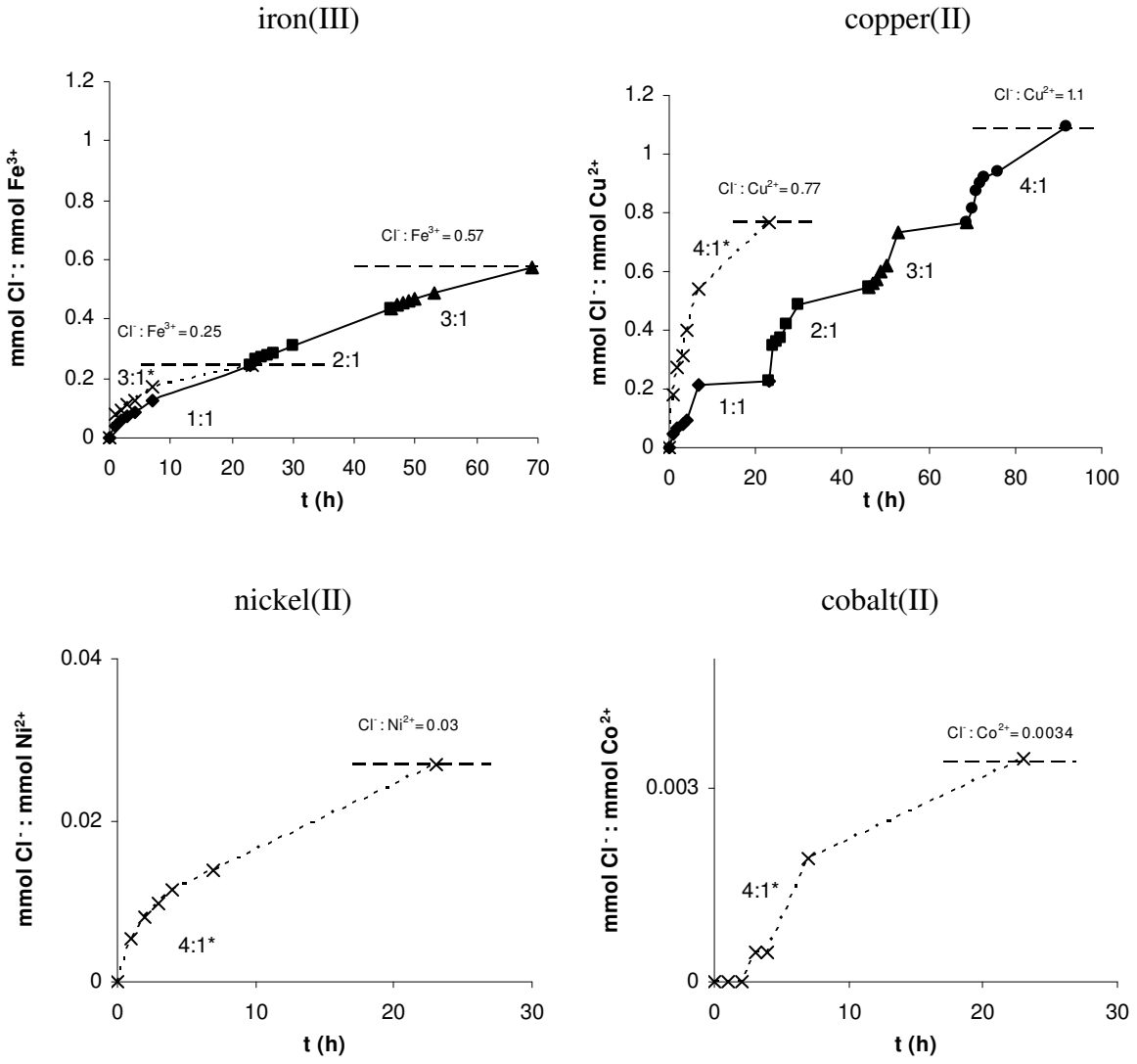

Figure 4-25. Release of chloride ions as a function of time during complexation of $FeCl_3$, $CuCl_2$, $NiCl_2$ or $CoCl_2$ with LIX 860-I in anhydrous media.

Iron(III)

The behaviour of LIX 860-I towards iron(III) is somewhat different compared to the extractants already discussed. A slower release of hydrogen chloride was observed with LIX 860-I. In the case of iron(III), the curve of the first step of the stepwise showed the same trend as curve of the direct procedure. Approximately the same Cl^-:Fe^{3+} ratio was obtained after 23 hours for both procedures (Cl^-:Fe^{3+} ratio = 0.24 – after first step of stepwise procedure – and Cl^-:Fe^{3+} ratio = 0.25 after direct procedure). Finally, a Cl^-:Fe^{3+} ratio of 0.57 was reached on completion of the stepwise procedure. The curves also show that a longer reaction time can influence the extractant:metal ratio. For that reason, it is not possible to predict the composition of the complexes, although with Job's method (see paragraph 4.2.3.5) an extractant:metal ratio of 3:1 was observed for iron(III).

Copper(II)

With copper(II), Cl^-:Cu^{2+} ratios of 1.1 and 0.77 were obtained during the stepwise and direct procedure, respectively. A longer reaction time can also influence the final extractant:metal ratio, though this trend is less strongly compared to iron(III).

Nickel(II) and cobalt(II)

Nickel(II) and cobalt(II) showed again only limited complexation.

UV-VIS absorption spectra

The UV-VIS absorption spectra of LIX 860-I and its iron(III) complexes are shown in Figure 4-26. No spectra are included of nickel(II) and cobalt(II) due to the limited release of hydrogen chloride. For copper(II) spectra, no marked differences were found between the different extractant:metal ratios.

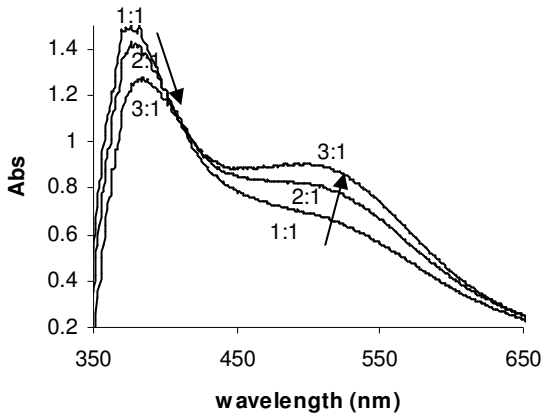

Figure 4-26. Absorption spectra of the iron(III) complexes during the stepwise procedure with LIX 860-I.

The intensity of the absorption band at 375 nm decreased with a higher extractant:metal concentration ratio. At the same time, a new band appeared (maximum at 510 nm). The absorption spectra clearly show a gradual evolution in the complex formation during the stepwise procedure as was also indicated by the analysis of the chloride ions. A longer reaction time is necessary to identify the composition of the complex at equilibrium.

FT-IR spectra

The FT-IR spectra of LIX 860-I and its iron(III) complex are shown in Figure 4-27. Two regions of the FT-IR spectra of LIX 860-I and its iron complex (3:1 extractant:metal ratio of stepwise procedure) are shown.

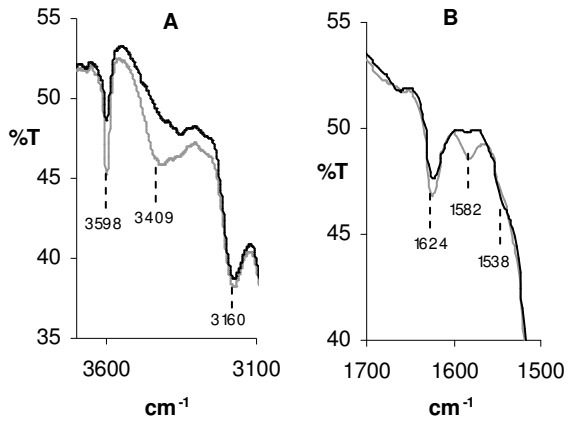

Figure 4-27. FT-IR spectra of LIX 860-I (grey) and Fe(III)-LIX 860-I complex (**black**).

The peak at 3598 cm^{-1} in Figure 4-27A can be ascribed to the free oximino hydroxyl group, while the peaks at 3409 and 3160 cm^{-1} are due to inter- and intramolecular bonded OH groups respectively [4_22]. The sharp band at 3160 cm^{-1} is due to intramolecular hydrogen bonding in which the phenolic proton is bonded to the nitrogen of the oxime group (see Figure 4-28). After complexation, the intensity of the band at 3409 cm^{-1} in Figure 4-27A diminished. The band at 1624 cm^{-1} (wavenumber range of 1700-1500 cm^{-1}) of the spectrum of LIX 860-I is due to the C=N stretching vibration (see Figure 4-27B) [4_22].

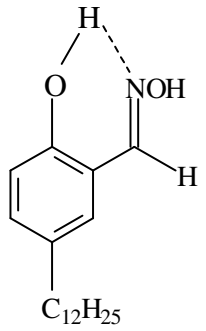

Figure 4-28. Intramolecular hydrogen bonding with LIX 860-I

In the case of copper(II), the same FT-IR spectrum was obtained as shown in Figure 3-25. Furthermore, no marked differences were observed between the spectra of the complexes of the different steps of the stepwise procedure.

Nickel(II) and cobalt(II) spectra are not included due to the limited complexation.

4.3.3. Influence of the actual amount of metal ion dissolved in the reaction mixture on the $Cl^-:M^{n+}$ ratio

During the progress of the experimental work, it was observed that the metal salt was not always completely dissolved in the hexane phase. Only in the case of D2EHPA, the total amount of iron(III) was completely dissolved for both procedures (after two hours). Therefore, 25 mL of the hexane phase at the end of step 1 (1:1) of the stepwise procedure of a new experiment and on completion of the direct procedure was stripped with 25 mL H_2SO_4 (3 $mol.L^{-1}$) in the case of iron(III) and copper(II) extraction with CYANEX 272, CYANEX 302, CYANEX 301 and LIX 860-I. Determination of the metal concentration in these acidic phases makes it possible to have a better insight in the effective extractant:metal ratio. In Table 4-16, an overview is given of the amount of metal dissolved in the hexane phases in the case of iron(III) and copper(II), expressed in percentage of the amount of added metal ion (1.25 mmol) as well as the effective $Cl^-:M^{n+}$ ratios.

The dissolution of the metal ion depends upon the ease of metal extraction. Therefore, the lowest deviations on the $Cl^-:M^{n+}$ ratio were found for iron(III) with D2EHPA and CYANEX 272, and for copper(II) with LIX 860-I (direct procedure). Major differences were found for CYANEX 302 and CYANEX 301. Taking the actual amount of dissolved metal into consideration, effective $Cl^-:M^{n+}$ ratios higher than 1:1 (or equal) were obtained for the stepwise procedures of iron(III) with D2EHPA, CYANEX 272, 302 and 301 and for the direct procedure of iron(III) with D2EHPA and CYANEX 301. So, not only $[FeCl_2L]$ complexes can be formed, but also $[FeClL_2]$ and $[FeL_3]$ complexes may be present. In the case of copper(II), $Cl^-:M^{n+}$ ratios higher than 1:1 were only noticed with CYANEX 301. The determination of the effective $Cl^-:M^{n+}$ ratio in the case of CYANEX 301 is however more difficult to calculate. Due to the high stability of the complexes with CYANEX 301, the hexane phases of comparable experiments were evaporated, followed by a destruction with concentrated sulfuric acid. However, no effective $Cl^-:M^{n+}$ ratio is calculated because of a still too low recovery. In the case of copper(II) and CYANEX 302, the stripping results were also extremely low, indicating that a destruction is necessary to define a more justified ratio.

Table 4-16. Influence of the actual amount of metal ion dissolved in the hexane phase on the $Cl^-:M^{n+}$ ratio.

Extractant	Water-free circumstances					
	$Cl^-:M^{n+}$		% metal dissolved		effective $Cl^-:M^{n+}$	
	1:1	D.P.[1]	1:1	D.P.[1]	1:1	D.P.[1]
D2EHPA						
Fe(III)	1.0	1.6	100	100	1.0	1.6
Cu(II)	0.04	0.10	-	6.4	-	-
CYANEX 272						
Fe(III)	0.90	0.30	87	93	1.0	0.32
Cu(II)	0.06	0.03	14	37	0.43	0.08
CYANEX 302						
Fe(III)	0.86	0.62	61	86	1.4	0.72
Cu(II)	0.85	0.53	8 [2]	5 [2]	-	-
CYANEX 301						
Fe(III)	0.70	1.4	42 [3]	64 [3]	1.7	2.2
Cu(II)	0.85	1.6	31 [3]	24 [3]	-	-
LIX 860-I						
Fe(III)	0.24	0.25	58	67	0.43	0.37
Cu(II)	0.23	0.77	45	98	0.51	0.79

[1] D.P.: result of direct procedure
[2] copper complexes too strong for stripping with 3 $mol.L^{-1}$ H_2SO_4
[3] complexes too strong: destruction with 18 $mol.L^{-1}$ H_2SO_4

4.3.4. Conclusion about water-free experiments

The results of iron(III) demonstrated that complexation of one extractant molecule proceeds very fast and involves the presence of two chloride ions in the metal complex. The further exchange of a chloride ion by another extractant molecule is also shown, although the reactions proceeded markedly slower compared to the first addition of extractant. These data support the idea that an extractant:metal ratio of 3:1 is not a necessary condition to extract iron(III). In an additional study, the hexane phase of a direct experiment of iron(III) with D2EHPA was contacted with slightly acidified aqueous phases. A complete release of chloride ions to the aqueous phases as well as nearly zero stripping of iron(III) was observed. Furthermore, the sulfate and nitrate concentrations in the aqueous phases did not change during shaking. Also a decrease in pH was noticed. These experiments prove the preference of iron(III) to coordinate with hydroxyl groups instead of chloride, sulfate or nitrate, as has already been found during the Job's method study.

Considering copper(II), the complexation of one extractant molecule around the metal ion proceeded also quite fast if CYANEX 302, CYANEX 301 or LIX 860-I was applied in the complexation process. The further exchange of a chloride ion was also markedly slower. In general, the same tendency was found as for iron(III). The results showed that an extractant:metal ratio of 2:1 is not a necessary condition to extract copper(II).

An important remark is that a lower amount of hydrogen chloride evolved in the presence of the CYANEX reagents during the direct procedure as compared to the stepwise procedure for copper(II) and iron(III) (except for CYANEX 301), this in contradiction to the results obtained with D2EHPA. Possible interactions between free extractant molecules or metal complex and HCl and/or the different stoichiometries which are preferred depending on the type of extractant may explain the difference in release of hydrogen chloride.

As far as nickel(II) and cobalt(II) are concerned, only small releases of hydrogen chloride were noticed.

As experimental work progressed, it was observed that not always the total metal salt was dissolved in the hexane phase. In fact, the dissolution of the metal ion depends upon the ease of metal extraction. Determination of the actual amount of metal dissolved in the hexane phases through stripping of the organic complexes showed therefore the lowest deviations on the $Cl^-:M^{n+}$ ratio in the case of the complexation of iron(III) with D2EHPA and CYANEX 272 and for copper(II) with LIX 860-I (direct procedure). The high strength of the complexes of CYANEX 302 and 301, especially with copper(II), limits an efficient determination of the real extractant:metal ratios.

4.4. COMPARISON OF JOB'S METHOD AND WATER-FREE EXPERIMENTS

In Table 4-17, a comparison is made between the extractant:metal ratios defined with Job's method and the results obtained in anhydrous media. A complete comparison is only possible for iron(III) and copper(II), because no effective $Cl^-:M^{n+}$ ratios were defined for nickel(II) and cobalt(II).

The data with Job's method showed an extractant:metal ratio of 1:1 or the involvement of hydroxyl groups in the extraction process of iron(III) with D2EHPA and CYANEX 272. The experiments under water-free conditions also showed that an extractant:metal ratio of 3:1 is not a necessary condition to extract iron(III).

Table 4-17. Comparison of Job's method and procedure under water-free circumstances

Extractant	Job's method	Water-free circumstances	
		1:1	D.P.[1]
	$HL:M^{n+}$ (M^{n+}=1)	$Cl^-:M^{n+}$ (M^{n+}=1)	$Cl^-:M^{n+}$ (M^{n+}=1)
D2EHPA			
Fe(III)	1	1.0	1.6
Cu(II)	2	-	-
Ni(II)	2		
Co(II)	2		
CYANEX 272			
Fe(III)	1	1.0	0.32
Cu(II)	2	0.43	0.08
Ni(II)	-		
Co(II)	2		
CYANEX 302			
Fe(III)	2	1.4	0.72
Cu(II)	-	-	-
Ni(II)	4		
Co(II)	4		
CYANEX 301			
Fe(III)	4	1.7	2.2
Cu(II)	2 or 4	-	-
Ni(II)	4		
Co(II)	2		
LIX 860-I			
Fe(III)	3	0.43	0.37
Cu(II)	2	0.51	0.79
Ni(II)	2		
Co(II)	3		

[1] D.P.: result of direct procedure

In fact, 1:1 extractant:metal ratios are quite easily achieved, although higher ligand coordination was also observed under water-free circumstances. $[FeCl_2L]$ complexes were formed, but also the existence of $[FeClL_2]$ and $[FeL_3]$ was assumed.

In the case of copper(II), nickel(II) and cobalt(II), the extractant:metal ratios defined with Job's method gave no indications of the participation of other anions in the respective extraction processes, besides the possible solvatation by water or neutral ligand molecules in the case of nickel(II) and cobalt(II). Under water-free conditions, 2:1 $Cl^-:M^{n+}$ ratios were not easily or were not at all achieved for these divalent metal ions. In fact, only limited

complexation was found for nickel(II) and cobalt(II) in anhydrous media, although the actual amount of metal ion dissolved in the hexane phases can have a marked influence on the effective $Cl^-:M^{n+}$ ratios. In addition, in the case of very strong complexes, such as copper(II)-CYANEX 301, effective ratios could not be determined. If the experiments with copper(II) are considered, where effective $Cl^-:M^{n+}$ ratios could be calculated (CYANEX 272 and LIX 860-I), lower ratios were found with the anhydrous procedure as compared to Job's method.

In fact, in both methods, the complexation characteristics are not completely the same. Nevertheless, the results of iron(III) with D2EHPA and CYANEX 272 with Job's method and the anhydrous procedure confirmed the fact that 1:1 extractant:metal complexes can be formed depending upon the extractant:metal ratio and type of extractant and metal ion, although higher ligand coordination is also possible and depends on the extraction circumstances.

4.5. CONCLUSION

Within this Chapter, two methods were applied to define the stoichiometry of the metal organic complexes of iron(III), copper(II), nickel(II) and cobalt(II) with D2EHPA, CYANEX 272, CYANEX 302, CYANEX 301 and LIX 860-I. The first method, Job's method, makes use of the fact that the optical properties of complexes differ from that of the constituents. The experiments have been carried out supposing that only monomeric extractant molecules were present. This spectrophotometric method was compared with a water-free procedure. By following up the release of hydrogen chloride during complexation, a correlation can be obtained with the number of extractant molecules present in the complexes.

Using Job's method, complexes with an extractant:metal ratio of 1:1 were found for iron(III) extraction with D2EHPA and CYANEX 272 instead of a ratio of 3:1, which would be expected on the basis of the electrical neutrality of the membrane phase. The absence of changes in chloride concentration in the aqueous phases during extraction inferred the participation of hydroxyl ions in the extraction mechanism. Higher extractant participation (2:1 or 4:1) was found in the case of the thiosubstituted organosphinic reagents. This can be explained either by the lower pH at which the experiments were performed or by the possible instability of these reagents. With LIX 860-I, an extractant:metal ratio of 3:1 was reached.

To eliminate any hydrolysis, a further study was made under water-free circumstances and a comparison was made with copper(II), nickel(II) and cobalt(II). The experiments under water-free conditions showed that 1:1 extractant:iron(III) complexes are easily formed. A further exchange towards higher extractant ratios was also observed, although the reaction proceeded slower. So, higher extractant coordination is also possible depending on the extractant type. In fact, both the existence of $[FeCl_2L]$, $[FeClL_2]$ and to a smaller extent $[FeL_3]$ was assumed.

In the case of copper(II), $[CuL_2]$ complexes have been distinguished with Job's method. In the case of cobalt(II) and nickel(II), 2:1 or 4:1 extractant:metal ratios were defined depending on the fact if solvatation of the metal complex (either by water molecules or by neutral extractant molecules) occurred or not.

The applied experimental procedure assumed only monomer species, although D2EHPA and CYANEX 272 are sometimes depicted as dimers. Therefore, the nickel(II)-D2EHPA extraction experiment was repeated with extractant concentrations calculated on the presence of totally dimeric units. The same maximum was obtained at a mole-fraction of metal ion around 0.33. Furthermore, the electronic spectra gave no indications of the formation of a different complex.

During the water-free experiments, $Cl^-:M^{n+}$ ratios of 2:1 were not achieved for copper(II), nickel(II) and cobalt(II). A major drawback of the anhydrous procedure is that the dissolution of the metal is depending upon the ease of extraction. Therefore, the $Cl^-:M^{n+}$ ratios were corrected with the real metal concentrations dissolved in the hexane solutions. If complexes are formed of high strength, viz. copper-CYANEX 301/302, the determination of the effective $Cl^-:M^{n+}$ ratios becomes very difficult. An easy stripping is therefore a prerequisite for calculating the effective extractant:metal ratio. Another prerequisite is a sufficient complexation rate to improve the accuracy of the method. Especially in the case of nickel(II) and cobalt(II), it was observed during the experimental work that only a small fraction of metal salt was dissolved in the reaction mixture. Another parameter which may affect the extractant:metal ratio is the ease of release of hydrogen chloride during the experimental process. This can be different for the various extractants and experimental circumstances.

In general, it can be stated that Job's method gives a more representative view on the stoichiometry of the metal organic complexes during liquid-liquid extraction compared to the water-free procedure. This last method however can be used to declare any unusual complexation behaviour, as observed during the extraction of iron(III) with D2EHPA and

CYANEX 272. Both methods confirmed that the formation of 1:1 neutral extractant:iron(III) complexes are possible through hydrolysis of iron(III). The extent of hydrolysis depends on the extraction circumstances.

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Chapter 5

PRACTICAL APPLICATION: RECOVERY OF NICKEL(II) WITH SUPPORTED LIQUID MEMBRANES

Chapters 3 and 4 were mainly dealing with the more fundamental aspects of the extraction or complexation process, viz. influence of aqueous and organic phase additives on the extraction mechanism and the determination of the stoichiometry of the metal organic complexes. In this Chapter, the recovery of nickel(II) with the Supported Liquid Membrane technology is studied. Several promising liquid ion exchangers for nickel(II) extraction are evaluated. In addition, the transport behaviour of nickel(II) is compared with the transport behaviour of an alkaline earth metal ion, viz. magnesium(II) in order to gain insight in the selectivity of these liquid ion exchangers. In a second study, experiments are performed on effluents created by the metal finishing industry to show whether the PARCOM levels for nickel(II) can be reached [5_1]. This work was carried out in the context of the Brite-EuRam project SERENI (SElective REcuperation of NIckel from industrial effluents) [5_2].

The Paris Commission has adopted PARCOM-Recommendation on Best Available Techniques and Best Environmental Practice, as mentioned already in Chapter 1. Many companies foresee problems when they keep on cleaning their waste water with the conventional environmental technologies due to the decrease of the discharge reference values. The limit for nickel(II) emission in waste water according to the PARCOM-Recommendation 92/4 is 0.5 $mg.L^{-1}$ [5_1]. The "Supported Liquid Membrane (SLM)" technology results into strongly reduced metal waste disposal and complies with the PARCOM requirements: reducing and avoiding waste and the recovery of valuable products (see also Chapter 1). All these advantages imply that SLM seems a useful technique for the removal and recovery of nickel(II).

The first step in developing a Supported Liquid Membrane system for a specific metal ion aims to define the composition of the liquid membrane. The choice of the extractant (or even mixed extractant system) is the key factor for a successful operation.

The most promising liquid ion exchangers for the extraction of nickel(II) can be divided into three major groups:

1. organophosphorous acid derivatives [5_3-5_6]
2. hydroxyoximes [5_5, 5_7-5_11]
3. and macrocyclic compounds [5_12].

Organophosphorous acid derivatives

An example of an organosphosphoric acid is D2EHPA [5_3-5_6], which can be used separately or in combination with other extractants in order to obtain synergistic enhancements. From the pH-isotherms of D2EHPA, which are depicted in Figure 2-16, it can be seen that D2EHPA is able to extract nickel(II) quantitatively at a pH of 5. However, D2EHPA is also able to extract magnesium(II) at this pH level.

Another type of organophosphorous acids are the organophosphinic acids (e.g. CYANEX 272). In the presence of CYANEX 272, the pH-isotherm of nickel(II) is shifted to higher pH values (pH > 6) (see also Figure 2-16). Replacing one oxygen donor by a sulfur atom, viz. CYANEX 302, leads to a marked shift of the pH-isotherms to lower pH values (pH 3-5). In addition, organophosphinic acids (especially the sulfur-substituted organophosphinic acids CYANEX 302 and CYANEX 301) are expected to show a better selectivity for transition metals, e.g. nickel(II), over alkaline earth metals, e.g. magnesium(II) [5_6].

Hydroxyoximes

As far as hydroxyoximes are concerned, aliphatic as well as aromatic types have the ability to extract nickel(II) [5_5, 5_7-5_11]. An example of an aliphatic oxime is decanaloxime (DOX) [5_7-5_9, 5_11]. LIX 860-I and LIX 84-I are examples of aromatic hydroxyoximes [5_5]. An extensive discussion of these types of reagents has been given in paragraph 2.2.3.1. The pH-isotherms of LIX 84-I (Figure 2-14) show that nickel(II) can be extracted at a pH above 4 [5_5]. Also derivatives of hydroxyoximes, viz. vicinal dioximes (see Figure 5-1) were investigated for nickel(II) extraction [5_10]. However, these extractants have only limited solubility in most organic diluents [5_10].

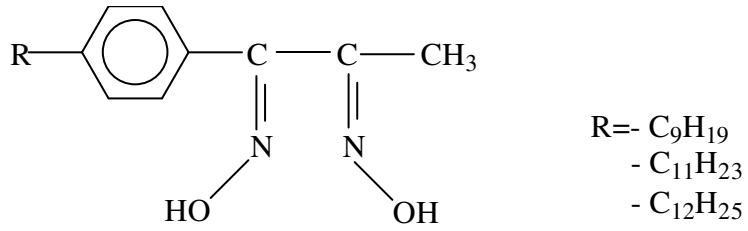

Figure 5-1. Structure of vicinal dioximes

Mixtures of organophosphorous acids and hydroxyoximes

The two groups of extractants already discussed (organophosphorous acid derivatives and hydroxyoximes) show however only a limited transport of nickel(II) [5_7-5_9, 5_11]. Therefore, combinations of these two types of extractants were often studied during the past in order to reach an efficient extraction system for nickel(II) [5_7-5_9, 5_11]. Synergistic enhancements of extraction of divalent transition metal ions were found with the oximes of aliphatic aldehydes and organophosphorous acids [5_7-5_9, 5_11]. A thorough discussion about the application of mixed extractant systems has been provided already in paragraph 2.2.4. Degradation of these aliphatic oximes through the acidic strip solutions limits however the usefulness of these reagents [5_8]. Therefore, the use of an aromatic hydroxyoxime, viz. LIX 860-I or LIX 84-I, in combination with an organophosphorous acid reagent opens perspectives for nickel(II) extraction with SLM. In Chapter 3, preliminary liquid-liquid extractions showed already a synergistic enhancement of nickel(II) extraction when using a mixture of D2EHPA and LIX 860-I as carrier system (see Figure 3-7). This synergistic enhancement was not observed in the case of magnesium (see Figure 3-23).

Macrocyclic compounds

A third group of promising liquid ion exchangers are the macrocyclic extraction reagents [5_12]. Extended series of tetraazamacrocyles form nickel(II) complexes. However, square planar complexes with nickel(II) must be avoided. The complex is thermodynamically too stable, which makes decomplexation too slow. N-cetylcyclam forms such a strong square planar complex with nickel(II) [5_12]. The cyclam donicity was therefore weakened by

changing the cetyl function into a tosyl function to obtain tosylcyclam (see Figure 5-2). The SO_2-group is thought to reduce the donating tendencies of the adjacent nitrogen atom [5_12].

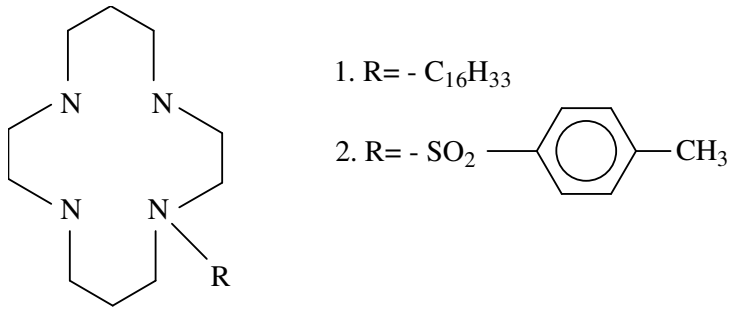

Figure 5-2. Structure of N-cetylcyclam (1) and 1-(4-tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane (Tosylcyclam) (2)

A major drawback of macrocylic extraction reagents is their limited commercial availability, especially if a good solubility in kerosene is a prerequisite in order to obtain a stable Supported Liquid Membrane system.

Summarized, it can be stated that a mixed extractant system of an organophosphorous acid and an aromatic hydroxyoxime shows the most promising perspectives for nickel(II) extraction. Therefore, the use of salicylaldo- or ketoximes in combination with organophosphoric or organophosphinic acids for nickel(II) extraction is extensively studied in this Chapter. Furthermore, a comparative study is provided with the extraction behaviour of magnesium(II). Preliminary experiments were carried out by means of convential extraction methods, viz. liquid-liquid extraction. The most efficient mixtures of extractants can then be investigated in a SLM lab-scale environment. At the end of this Chapter, tests will be made with real effluent streams to show whether the PARCOM-limit of nickel(II) can be reached.

5.1. LIQUID-LIQUID EXTRACTIONS

The extractant is dissolved in a hydrocarbon diluent (kerosene) and is brought into contact with an aqueous solution of the metal salt. The reaction takes place at the interface and the metal ion is transferred into the organic phase until equilibrium is reached. The efficiency of the extraction reaction can be expressed by means of the distribution coefficient k, which is calculated according to Equation (2-14) or by means of the extraction percentage, which is calculated according to Equation (2-15).

5.1.1. General procedure

Stock solutions of nickel(II) were prepared with the appropriate sulfate salt. Kerosene was applied as organic diluent for the extractants. Kerosene, a typical industrial solvent, is often used in liquid membrane processes because of its low volatility. Its physico-chemical properties at 25° C were already shown in Table 2-3. The properties of the extraction reagents are described in Annex A.

In a separation funnel of 100 mL, 20.00 mL nickel(II) solution - 8.50 x 10^{-3} mol.L^{-1} (or 500 mg.L^{-1}) - with an initial pH of 4.5 (buffered with 0.25 mol.L^{-1} (Na, H)Ac, unless stated otherwise) was added to 20.00 mL of an extractant solution containing 0.04 mol.L^{-1} extractant diluted with kerosene Shellsol D100 (Shell Chemicals) giving a mole ratio HL/Ni(II) of 5/1. 4.10 x 10^{-3} mol.L^{-1} (or 100 mg.L^{-1}) magnesium(II), also prepared with the appropriate sulfate salt, was added to the nickel(II) solution.

At room temperature, the funnel was placed into a shaker at 305 rpm for 10 minutes. After separation of the two phases, the nickel(II) and magnesium(II)s concentration in the aqueous phases were measured by Atomic Absorption after appropriate dilution.

5.1.2. Extraction efficiency of commercial hydroxyoxime and organophosphorous acid liquid ion exchangers for nickel(II) extraction

At first, the extraction performance of different commercial hydoxyoximes and organosphosphorous acids for nickel(II) was investigated at two different pH levels, namely pH 5.0 and 7.0. No buffer was added to the feed solution.

The results are shown in Figure 5-3. The extraction performance is expressed in this first experimental paragraph by means of extraction percentages in order to display the results

in the Figure in a representative way. The corresponding distribution coefficients are listed in Annex E, Table E-1.

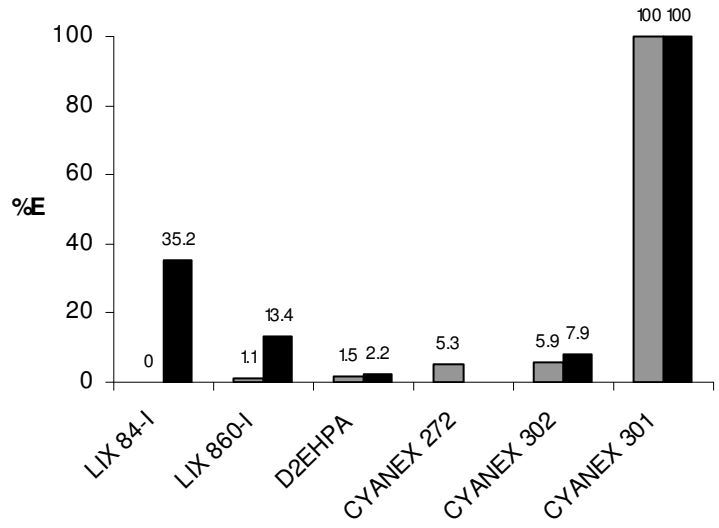

Figure 5-3. Extraction of Ni(II) with commercial hydroxyoxime and organophosphorous acid liquid ion exchangers at an initial pH of 5.0 (■) and 7.0 (■).

CYANEX 301, a dithiophosphinic acid, is the only extractant showing a sufficient extraction of nickel(II). An important drawback of this type of extractant in contrast to the other investigated ligands is that it forms a very strong complex with nickel(II), resulting in a difficult decomplexation [5_2]. Sulfuric acid (1 mol.L^{-1}) only stripped 15% of the nickel(II) amount [5_2]. Similar observations could be made with hydrochloric acid [5_2]. Several ways to improve the stripping of nickel(II) did not result in a useful decomplexation process. Only the addition of an organic phase modifier to the extractant solution, such as isotridecanol (up to 60%), improved the stripping characteristics although the addition of a more polar solvent is not favourably for the long-term stability of a liquid membrane phase [5_2].

When the other investigated extractants are compared, the LIX reagents show some extraction of nickel(II) at pH 7.0. At pH 5.0, the extraction efficiency was very poor. This was also the case with the organophosphorous acid reagents, but at both pH levels.

The first screening did not predict good perspectives for the extraction of nickel(II). In literature was found that mixed extractant systems can improve the extraction rate of nickel(II) [5_7-5_9, 5_11]. Therefore, in the succeeding paragraphs, further investigations are

focussed on the combination of two types of extraction reagents, namely a hydroxyoxime and an organophosphorous acid.

5.1.3. Extraction efficiency of mixed extractant systems

In the succeeding paragraphs, the influence of the type of hydroxyoxime and type of organophosphorous ligand on the extraction efficiency of nickel(II) is discussed and a comparison is made with the extraction behaviour of magnesium(II).

The efficiency of the extraction system will be expressed as a function of the distribution coefficient k, which can be calculated according to Equation (2-14).

5.1.3.1. Influence of a mixture of LIX 84-I and D2EHPA on the extraction efficiency of nickel(II) and magnesium(II)

The extraction performance of a mixture of 0.04 mol.L^{-1} D2EHPA and 0.04 mol.L^{-1} LIX 84-I has been compared to the separate extraction performance of D2EHPA (0.04 mol.L^{-1}) and LIX 84-I (0.04 mol.L^{-1}). The results are shown in Figure 5-4. Complete extraction data are given in Annex E, Table E-2.

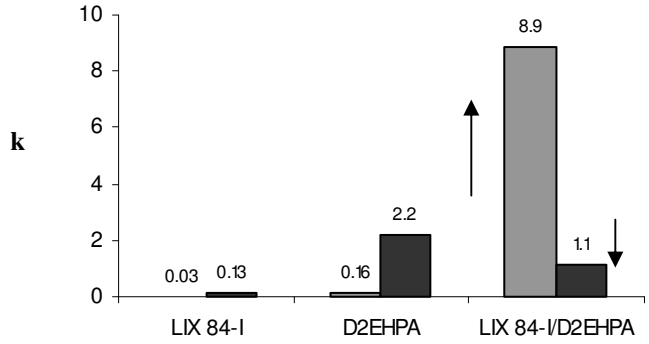

Figure 5-4. Influence of a mixture of D2EHPA and LIX 84-I on the distribution coefficient k of nickel(II) (■) and magnesium(II) (■) + comparison with separate extraction performance of D2EHPA and LIX 84-I.

A higher distribution coefficient is obtained for magnesium(II) compared to nickel(II) with D2EHPA as extractant. LIX 84-I shows a low affinity for both metal ions. Combining

D2EHPA with LIX 84-I improved the distribution coefficient of the nickel ion and decreased the amount of magnesium(II) extracted (see arrows). This means that a significant favourable synergistic effect occurs during the extraction of nickel(II) when D2EHPA and LIX 84-I are combined.

5.1.3.2. Influence of the type of organophosphorous acid in the extractant mixture containing LIX 84-I and comparison with the extraction efficiency of a carboxylic acid

In this paragraph, related organophosphorous extractants and a carboxylic acid, Versatic 10, are now investigated in combination with LIX 84-I and a comparison is made with the extraction performance of D2EHPA in the reagent mixture. The results are shown in Figure 5-5. Versatic 10 was supplied by Shell Chemicals. Versatic 10 is a synthetic, highly branched-C10 tertiary carboxylic acid [5_13]. The properties of the extractant are described in Annex A. Extraction data are included in Annex E, Table E-3.

The distribution coefficient of nickel(II) follows the order: phosphoric >> monothiophosphinic > phosphinic > carboxylic acid.

The carboxylic acid showed limited results compared to the phosphoric and phosphinic acids. Versatic 10 is a weaker extractant, requiring a pH around 7 for efficient nickel(II) extraction [5_14]. Similar with D2EHPA, it is not particularly selective but its price is one of its most attractive features [5_14]. Considerable efforts have been made to increase the extractant's affinity for nickel(II) by the introduction of various modifiers although no particular success was achieved [5_14].

When the organophosphorous acid extractants are compared, the highest distribution coefficient of nickel(II) was reached with D2EHPA. Magnesium(II) was only extracted significantly when D2EHPA was present in the extractant mixture. CYANEX 302 shows a slightly higher extraction efficiency for nickel(II) compared to CYANEX 272. The removal of the alkoxy oxygens of the reagents (D2EHPA [$(RO)_2POOH$] versus CYANEX 272 [$(R)_2POOH$] and CYANEX 302 [$(R)_2PSOH$]) shortens the distance between the alkyl chains and the phosphoryl group [5_15]. This shorter distance reduces the stability of the nickel(II) complexes because of an overcrowding effect. This effect can also be observed by increasing the branching of the alkyl chains [5_15].

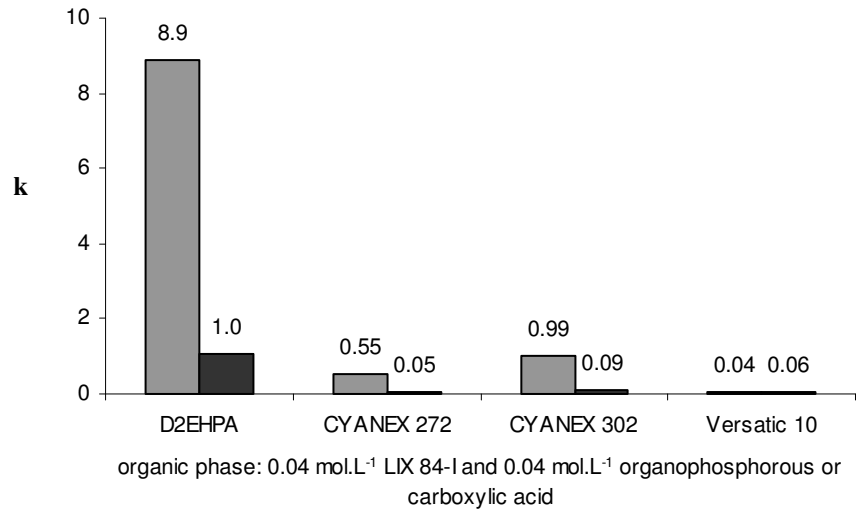

Figure 5-5. Distribution coefficient k of nickel(II) (■) and magnesium (■) with mixtures of LIX 84-I and different organophosphorous or carboxylic acid extraction reagents.

However, nearly no magnesium(II) is extracted in the presence of CYANEX 272 and CYANEX 302. These organophosphinic acids result in a slightly more selective extraction of nickel(II) over alkaline earth metal ions compared to D2EHPA.

5.1.3.3. Influence of the type of oxime in combination with CYANEX 302

Instead of LIX 84-I, another type of hydroxyoxime is now evaluated in combination with CYANEX 302 (see Figure 5-6 and Annex E, Table E-4).

LIX 860-I showed a slightly higher distribution coefficient for nickel(II) compared to LIX 84-I. On the other hand, a small increase of the distribution of magnesium(II) was also observed.

In literature [5_11], it was mentioned that the dominant factor in determining the extent of the synergistic effect is function of the steric hindrance of the oxime. This effect was more pronounced in the case of the ketoxime (methylsubstituent) compared to the aldoxime (substituent is hydrogen) [5_11]. This can explain the higher distribution coefficient obtained with the aromatic aldoxime in combination with an organophosphinic acid ligand.

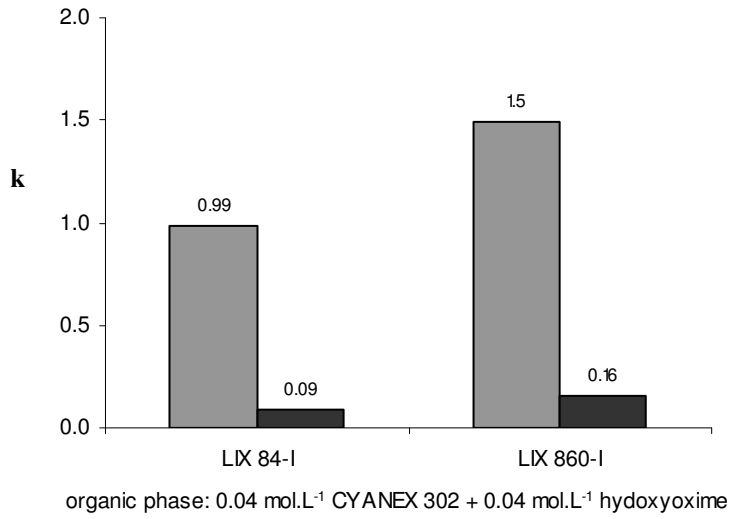

Figure 5-6. Influence of the type of hydroxyoxime on the distribution coefficient k of nickel(II) (■) and magnesium (■) in a mixed extractant system with CYANEX 302.

5.1.4. Conclusion about liquid-liquid extractions

At acidic pH, only CYANEX 301 showed a remarkable nickel(II) extraction. An important drawback of this extractant is its formation of highly stable complexes, which makes the stripping process very difficult. The difficult decomplexation and stability problems limit therefore the usefulness of CYANEX 301 as extraction reagent for nickel(II).

Liquid-liquid extractions with other organophosphorous acid extractants and hydroxyoximes showed only restricted distribution coefficients for nickel(II). However, combining organophosphoric acids or phosphinic ones with aldo- and ketoximes improved the extraction efficiency of nickel(II). Replacing D2EHPA by organophosphinic acids, such as CYANEX 302 or CYANEX 272 in the reagent mixture, increased the selectivity of the extraction of nickel(II) compared to alkaline earth metals, viz. magnesium(II), but nickel(II) extraction was lower. Furthermore, the influence of the type of hydroxyoxime in combination with D2EHPA was investigated. LIX 860-I showed a slightly higher distribution coefficient for nickel(II) compared to LIX 84-I.

5.2. SUPPORTED LIQUID MEMBRANES

In the succeeding paragraphs, the influence of the type of hydroxyoxime and type of organophosphorous acid in mixed extractant systems will be investigated in a SLM lab-scale environment.

Different configurations can be used as far as the support membrane is considered in SLM, as mentioned in paragraph 2.4. The two most useful geometries are flat membranes and hollow fiber modules. For industrial purposes, the use of a planar geometry is not very effective since the ratio of surface area to volume is too low. However, for receiving a first indication on the efficiency of the extraction process, planar of flat membranes can be very useful. Therefore, preliminary experiments were performed with flat membranes. The different procedures and results are discussed in the succeeding paragraphs.

5.2.1. Flat membranes

Before starting the SLM experiments, a screening was made of the commercial available flat membranes. The reason for a Supported Liquid Membrane to become instable is the loss of the liquid membrane phase (extractant and/or solvent) out of the pores of the support [5_16]. This loss of extractant and/or membrane solvent can be due to several parameters, such as a pressure difference over the membrane, solubility of extractant and membrane solvent in adjacent feed and strip solutions, wetting of support pores by the aqueous phases, blockage of support pores by precipitation of the extractant, the presence of an osmotic pressure gradient over the membrane or emulsion formation of the liquid membrane phase in water induced by lateral shear forces (see also paragraph 2.7) [5_16].

When the pressure difference across the membrane exceeds a critical value, the liquid membrane phase is pushed out of the pores of the support. The critical displacement pressure P_c for an SLM can be defined as the minimum transmembrane pressure required to displace the impregnating phase out of the largest pore of the membrane– see also Equation (2-36). Therefore, the critical displacement pressures were determined for commercial available membranes. The critical displacement pressure was measured by applying an increasing pressure on a water circuit closed with a test membrane, which was impregnated with kerosene. This test membrane was soaked in a transparent glass which was filled with kerosene. The pressure producing the first appearance of turbidity near the membrane, due to water droplets in the kerosene phase, was noted by visual observation.

The results are shown in Table 5-1. Furthermore, the measured break through pressures are plotted as a function of the pore size of the membranes in Figure 5-7.

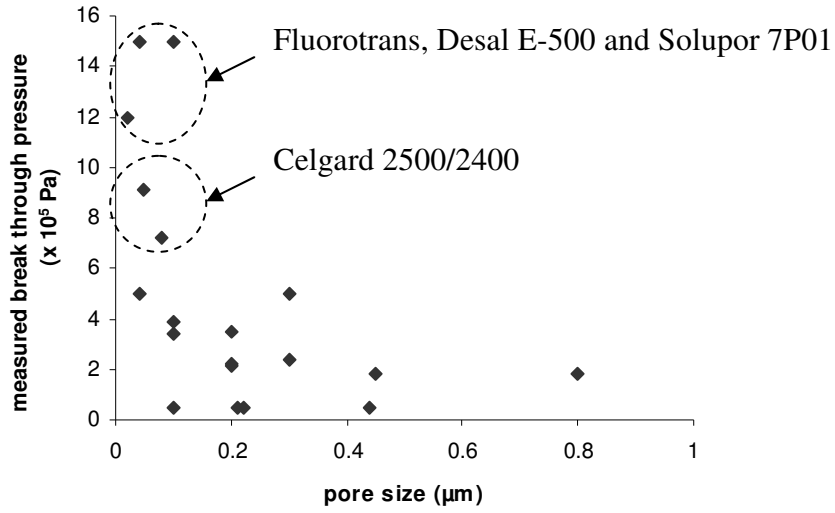

Figure 5-7. Plot of the measured break through pressures as a function of the pore size of the membranes

For three membranes (FluoroTrans – 0.02 µm (> 12 x 10^5 Pa), Desal E-500 and Solupor 7P01 (> 15 x 10^5 Pa)), the break through pressure was not detectable. Therefore, the maximum pressure which could be tested for these membranes is depicted in Figure 5-7 in order to compare the results in a representative way.

Also, the Celgard membranes showed satisfactory results. In general, the results show that the highest break through pressures were obtained with the membranes having the smallest pore size (Figure 5-7). Therefore, supports should be used with a small pore size (see also Laplace Equation (2-36)). Of course, the extent of the hydrophobicity of the support membrane is also important.

Table 5-1. Measurement of the critical displacement pressure of hydrophobic membranes.

Membrane	Manufacturer	Polymer	Mentioned pore size (µm)	Measured break through pressure (x 10^5 Pa)
FluoroTrans W	Pall-Gelman	PVDF	0.20	2.2
FluoroTrans	Pall-Gelman	PVDF	0.20	3.5
	Pall-Gelman	PVDF	0.04	5.0
	Pall-Gelman	PVDF	0.02	> 12
Celgard 2500	Hoechst	PP	0.08	7.2
Celgard 2400	Hoechst	PP	0.05	9.1
Micro PES 2F	Akzo Nobel	Polyethersulfone	0.20	2.1
Micro PES 1F EL	Akzo Nobel	Polyethersulfone		3.0
Micro PES 1F PH	Akzo Nobel	Polyethersulfone	0.10	3.4
Accurel 1E PP	Akzo Nobel	PP	0.10	3.9
Desal JW	Desalination Systems	PVDF	0.30	2.4
Desal E-500	Desalination Systems	polysulfone	0.04	> 15
Tetratex #6503	Tetratec Europe	PTFE (polyester backing)	0.45	1.8
Tetratex #6523	Tetratec Europe	PTFE (PP backing)	0.44	0.5
Tetratex #6522	Tetratec Europe	PTFE (PP backing)	0.22	0.5
Tetratex #6521	Tetratec Europe	PTFE (PP backing)	0.21	0.5
Tetratex #6531	Tetratec Europe	PTFE (polyester backing)	0.10	0.5
Zitex A155	Norton Performance Plastics	PTFE	2-5	0.6
Solupor 7P20	DSM Solutech	Polyethylene	0.80	1.8
Solupor 7P03	DSM Solutech	Polyethylene	0.30	5.0
Solupor 7P01	DSM Solutech	Polyethylene	0.10	> 15
Isopore	Millipore	Polycarbonate	0.20	< 0.5
Fluoropore	Millipore	Teflon	0.20	< 0.5

Finally, Celgard 2400 was chosen as flat membrane for the experimental work (effective surface area: 0.0062 m^2). Besides their excellent product uniformity, strength and chemical stability, these polypropylene membranes with sub-micron porosity have an additional advantage that they are also commercial available in a hollow-fiber configuration. The characteristic properties of the Celgard membranes have been discussed in paragraph 2.4. The general procedure is discussed in the next paragraph.

5.2.1.1. General procedure

At first, the hydrophobic porous membrane, Celgard 2400 (area: 0.0062 m^2) needs to be impregnated with the mixture of the two ligands diluted in kerosene. The membrane was soaked in the extractant solution over night in a Petri-dish. Afterwards, the membrane was rinsed with deionised water to remove any excess of extraction reagent. Then, the flat membrane was clamped between the feed and the strip compartment. The experimental device is shown in Figure 5-8.

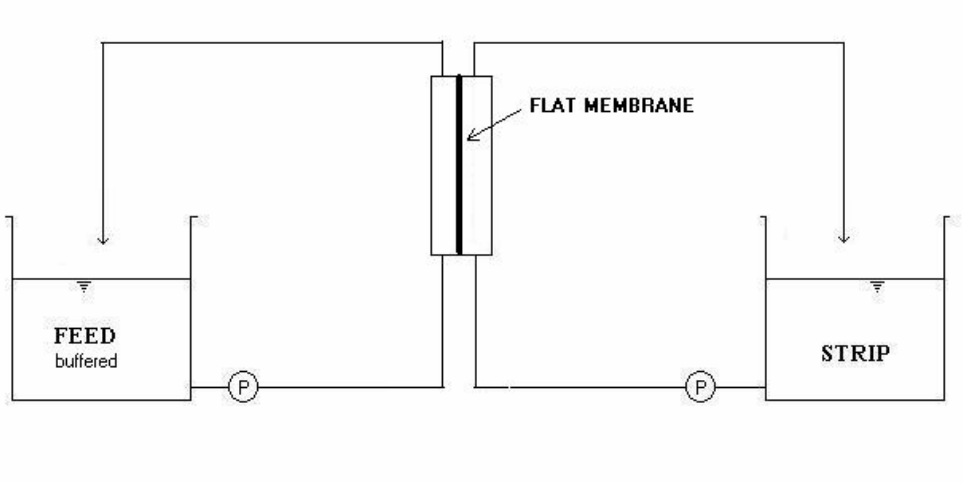

Figure 5-8. Experimental device with flat membrane

Equal extractant concentrations of 0.4 $mol.L^{-1}$ were applied in the extractant mixture, unless stated otherwise. The SLM experiments were performed at a higher concentration of extractant compared to the liquid-liquid extractions in order to achieve reasonable fluxes.

The experiment was set up by pumping feed (0.2 L) and strip (0.2 L) in the same direction along this membrane (recirculation). The feed containing 8.50 x 10^{-3} $mol.L^{-1}$ (500 $mg.L^{-1}$) nickel(II) was prepared with the appropriate sulfate salt and buffered at pH 4.5 by adding 0.25 $mol.L^{-1}$ (Na, H)Ac buffer. 4.10 x 10^{-3} $mol.L^{-1}$ (100 $mg.L^{-1}$) magnesium(II), prepared with the appropriate sulfate salt was added to the nickel solution. As strip solution, 1.5 $mol.L^{-1}$ H_2SO_4 was used.

The nickel and magnesium concentrations in the aqueous phases were measured by Atomic Absorption after appropriate dilution.

Fluxes of nickel(II) are calculated at both the feed and strip side according to Equation (2-34). The fluxes are included in Annex F.

Fluxes of magnesium(II) are only calculated at the strip side due to the low amounts of magnesium(II) transported across the membrane phase. The differences in magnesium(II) concentrations can be measured more accurately in the strip phase (at the start no magnesium(II) is present) compared to the small differences in concentrations in the feed phase (those concentrations will fluctuate around 100 $mg.L^{-1}$). As a consequence, the fluxes (strip side) of magnesium(II) will be displayed as a function of time and not in function of the feed concentration.

5.2.1.2. Influence of the type of hydroxyoxime and type of organophosphorous acid extraction reagent in a mixed extractant system on the nickel(II) and magnesium(II) flux

The liquid-liquid extraction results showed that mixtures of organophosphoric acids or –phosphinic acids and aldo- or ketoximes improved the distribution coefficient of nickel(II) compared to the extraction performance of the separate extractants. Therefore, these mixed extractant systems are now investigated in a Supported Liquid Membrane device containing a flat membrane.

At first, the influence of the type of organophosphorous acid reagent was investigated when combined with LIX 84-I as hydroxyoxime reagent. In Figure 5-9, the fluxes of nickel(II) (calculated at the feed and strip side) are displayed as a function of the feed concentration. Also additional information is given concerning the fluxes of magnesium(II) (calculated at the strip side) to gain further insight in the selectivity of the mixed extractant systems. The measurement data are included in Annex F, Table F-1.

Both the nickel(II) fluxes calculated at the feed and strip side show the same trend as shown in Figure 5-9. This was also noticed during the other experiments. Therefore, in the succeeding paragraphs, only de fluxes calculated at the strip side will be displayed.

The results depicted in Figure 5-9 show that the highest nickel(II) fluxes are obtained in the case of a mixture of LIX 84-I and D2EHPA. At the same time, magnesium(II) is extracted. The lower flux value of magnesium(II) after 20 hours (encircled) is due to the lower remaining magnesium(II) concentration in the feed phase at that time.

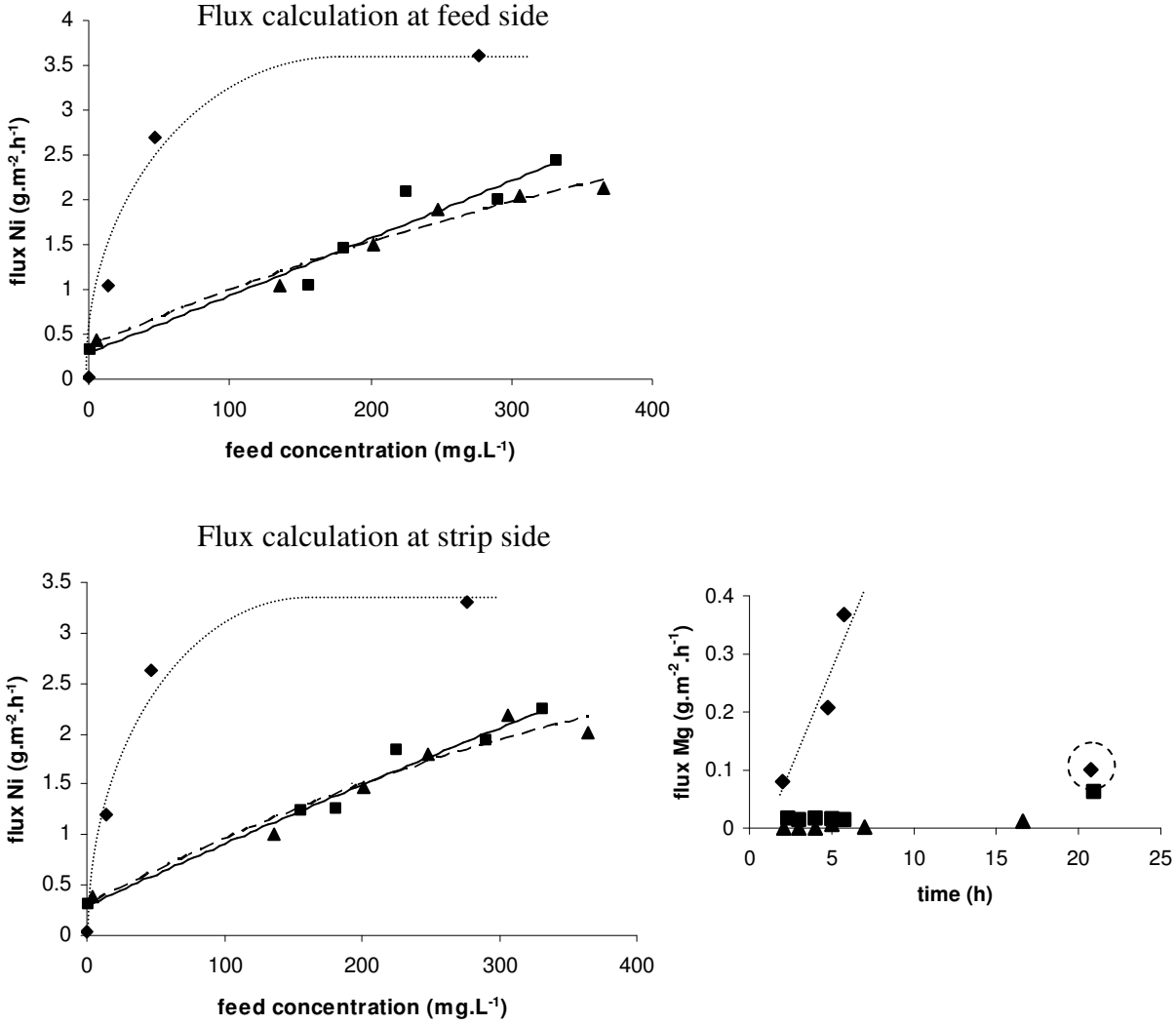

Figure 5-9. Influence of the type of organophosphorous acid on the fluxes of nickel(II) and magnesium(II) in combination with LIX 84-I as extraction reagent.
(♦, trendline: ……) D2EHPA; (■, trendline: –) CYANEX 272;
(▲, trendline: ------) CYANEX 302

Only small differences were observed between CYANEX 272 and CYANEX 302, although a slightly better selectivity was found for CYANEX 302 and LIX 84-I. A lower nickel(II) flux was obtained with CYANEX 302 in the reagent mixture compared to D2EHPA, but nearly no magnesium(II) was transported.

In a second set of experiments, another type of oxime, LIX 860-I, was investigated in combination with CYANEX 302. These results are displayed in Figure 5-10 (see also Annex F, Table F-1).

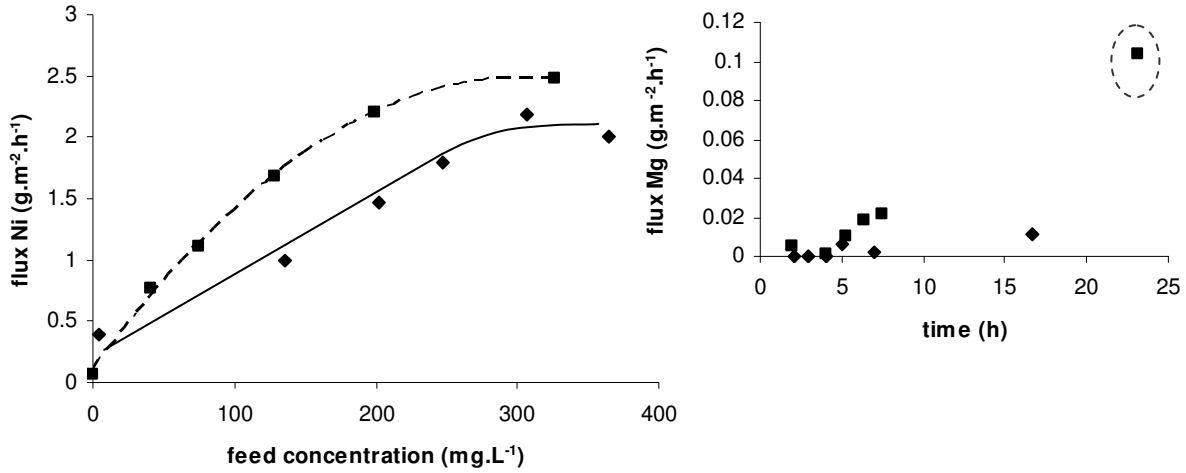

Figure 5-10. Influence of the type of hydroxyoxime on the fluxes of nickel(II) and magnesium(II) in combination with CYANEX 302 as extraction reagent.
(♦) LIX 84-I; (■) LIX 860-I

The mixture of CYANEX 302 and LIX 860-I showed a higher nickel(II) flux compared to the mixture of CYANEX 302 and LIX 84-I. At the same time, more magnesium(II) was transported. The high flux value of magnesium(II) after 23 hours (encircled) is due to the lower remaining nickel(II) concentration in the feed phase at that time (see also Annex F, Table F-1). Further experiments on pilot-scale SLM with a mixture of LIX 860-I and CYANEX 302 have shown that no magnesium(II) is transported into the strip phase if the nickel(II) concentration remains high enough (400-500 $mg.L^{-1}$) [5_17].

As can be concluded from the previous experiments, the highest nickel(II) fluxes were achieved with a mixture of LIX 84-I and D2EHPA. However, if a better selectivity against alkaline earth metal ions is needed, a mixture of LIX 84-I or LIX 860-I with CYANEX 302 is a better option.

5.2.2. Hollow fiber modules

Further experiments were made with hollow fiber modules instead of flat membranes. The influence of the carrier concentration will be investigated as well as the influence of the strip concentration. A mixture of LIX 860-I and CYANEX 302 is used as extractant solution. But first of all, the general procedure is described in the next paragraph.

5.2.2.1. General procedure

The experimental device for the hollow fiber modules is shown in Figure 5-11. Three liter feed solution (8.50 x 10^{-3} mol.L^{-1} or 500 mg.L^{-1} nickel(II) and 4.10 x 10^{-3} mol.L^{-1} or 100 mg.L^{-1} magnesium(II)) was circulated through the polypropylene hollow fibers (lumen side) of a Liqui-cel Membrane Contactor 5PCM-100 from Membrana (Celgard) (recirculation – flow rate of 20 L.h^{-1}). The contactor provides an effective surface area of 0.4 m^2. The pH of the feed was kept constant at 4.5 by adding a sodium hydroxide solution (pH control). The strip solution (l L) was circulated at the shell side (flow rate of 20 L.h^{-1}). Prior to the starting up of the analysis, the module was circulated with feed and strip solution during two hours, followed by a replacement of the feed and strip solution by a new solution. In this way, the extractant phase was loaded with metal ions at the start of the experiment.

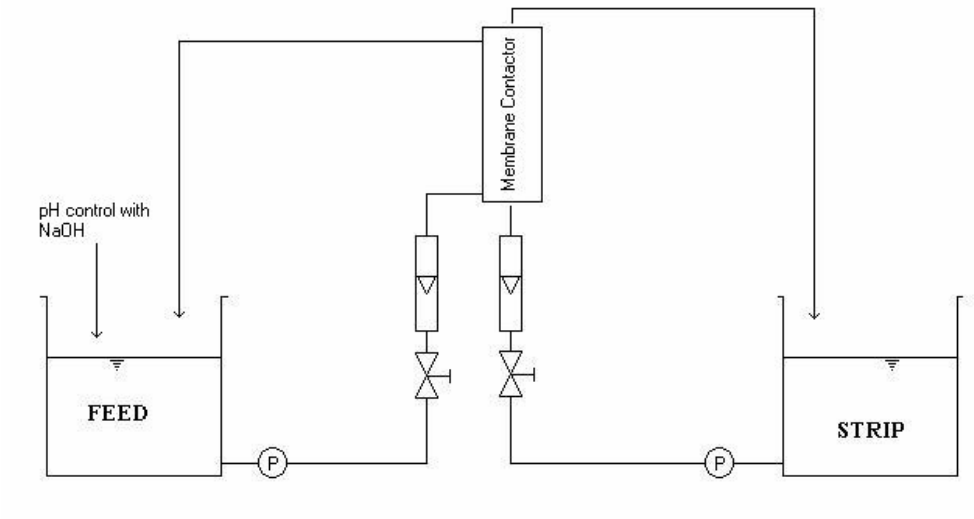

Figure 5-11. Experimental device with hollow fiber module

The nickel(II) and magnesium(II) concentrations in the aqueous phases were measured by AAS after appropriate dilution.

Fluxes of nickel(II) are calculated at both the feed and strip side according to Equation (2-34). Only the fluxes calculated at the strip side are displayed in the Figures. Both fluxes show the same trend and are included in Annex F (Tables F2-F3).

5.2.2.2. Influence of the acidity of the strip solution on the transport of nickel(II)

As strip solution, two different concentrations of sulfuric acid were applied, namely 1.5 mol.L^{-1} and 3 mol.L^{-1}. A mixture of 0.4 mol.L^{-1} LIX 860-I and 0.4 mol.L^{-1} CYANEX 302 was used as extractant solution. The results are shown in Figure 5-12. Measurement data are listed in Annex F, Table F-2.

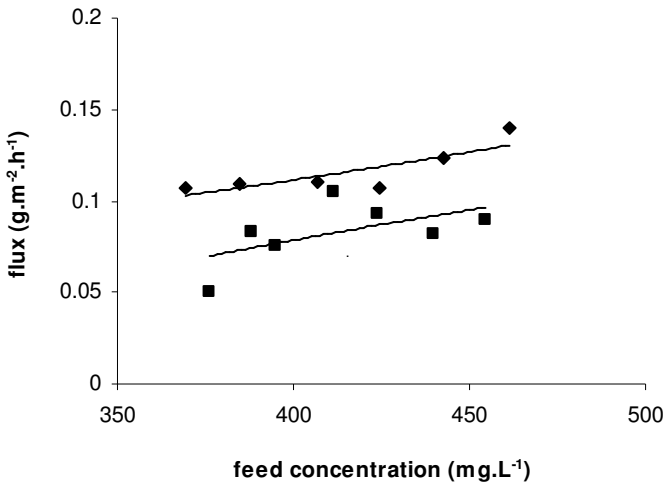

Figure 5-12. Influence of the acidity of the strip solution on the nickel(II) flux: (♦) 1.5 mol.L^{-1}; (■) 3 mol.L^{-1} sulfuric acid

Increasing the acidity of the strip solution did not improve the nickel(II) flux. On the contrary, with 3 mol.L^{-1} sulfuric acid, the nickel(II) flux showed a trend of slightly lower values compared to 1.5 mol.L^{-1} sulfuric acid. Therefore, 1.5 mol.L^{-1} will be used as strip solution during the further experimental work.

Furthermore, no magnesium(II) was transported into the strip solution.

5.2.2.3. Influence of the concentration of the carrier on the transport of nickel(II)

The concentration of each carrier in the extractant mixture was varied from 0.2 to 0.8 mol.L^{-1} (extractants always present with equimolar concentrations). The results are shown in Figure 5-13. Measurement data are listed in Annex F, Table F-3.

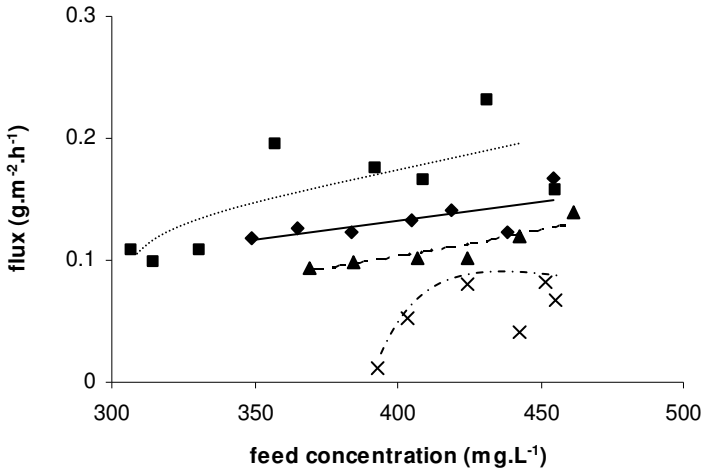

Figure 5-13. Influence of the carrier concentration on the flux of nickel(II): (♦, trendline: —) 0.8 mol.L^{-1}; (■, trendline: ……) 0.6 mol.L^{-1}; (▲, trendline: -----) 0.4 mol.L^{-1}; (×, …..) 0.2 mol.L^{-1} equimolar mixture of LIX 860-I and CYANEX 302.

Figure 5-13 reveals that there is a trend towards higher nickel(II) fluxes when the extractant concentration is increased. The highest fluxes were found around 0.6 mol.L^{-1} as concentration for each carrier in the extractant mixture. Raising the concentration up to 0.8 mol.L^{-1} showed a trend towards lower nickel(II) fluxes. At high extractant concentrations, steric hindrance or a higher viscosity of the liquid film can inhibit the metal transport through the liquid membrane.

5.2.3. Conclusion about SLM experiments

The experiments performed on lab-scale SLM-level have shown that the flux of nickel(II) depends on the type of hydroxyoxime or organophosphorous acid extractant present

in the extractant mixture. Higher nickel(II) fluxes can be obtained with D2EHPA compared to CYANEX 302 in a mixed extractant system with a hydroxyoxime. However, with CYANEX 302, a better selectivity towards alkaline earth metal ions was reached. On the other hand, when the hydroxyoxime type reagent is considered, the aldoxime – LIX 860-I – showed a trend towards slightly higher nickel(II) fluxes compared to LIX 84-I in the reagent mixture.

An increase of the concentration of the extractant (mixture of LIX 860-I and CYANEX 302) improves the nickel(II) flux. However, the increase of the carrier concentration is limited and this can be attributed to effects of steric hindrance and an increase of the viscosity of the liquid film. A maximum nickel(II) flux was found at a carrier concentration around 0.6 mol.L^{-1} Increasing the acidity of the strip solution from 1.5 to 3 mol.L^{-1} sulfuric acid did not improve the nickel(II) flux.

5.3. EXPERIMENTAL RUNS WITH REAL NICKEL(II) EFFLUENTS

In a further study, experiments were performed with real nickel(II) effluents in order to show that the PARCOM value of 0.5 mg.L^{-1} for nickel(II) can be reached. The effluents created by the metal finishing industry result from different types of nickel bath rinse solutions, which are used in industrial plating shops. The Watt's bath, the sulphamate bath and the electroless nickel bath are widely used for rapid plating of ductile nickel with high cathode and anode efficiencies. The general formulation of the three types of nickel(II) baths is described in Annex G.

The same experimental device was used as shown in Figure 5-11. The same general procedure was used as described in paragraph 5.2.2.1, except that a volume of 1 L nickel bath rinse solution was taken as feed solution and that the 'Liqui-cel' Membrane Contactor 5PCG-259 with an effective surface area of 1.4 m^2 was used for the experimental work. The organic phase existed of a mixture of 0.4 mol.L^{-1} LIX 860-I and 0.4 mol.L^{-1} CYANEX 302 diluted in kerosene. In paragraph 5.2.2.3, it was shown that a concentration of 0.6 mol.L^{-1} for each of the carrier in the extractant mixture resulted into higher nickel(II) fluxes compared to 0.4 mol.L^{-1}. However, it is expected that with a concentration of 0.4 mol.L^{-1}, the PARCOM-limit can be achieved as well. If a faster removal of nickel(II) is required, the concentration can be raised to 0.6 mol.L^{-1}.

Three types of nickel bath rinse solutions - Watt's bath, nickel sulphamate bath and electroless nickel bath - were used and compared to a synthetic nickel(II) solution containing approximately 8.50 x 10^{-3} mol.L^{-1} or 500 mg.L^{-1} nickel(II).

Figure 5-14 shows the evolution of the nickel(II) concentration in both feed and strip solutions as a function of time. Measurement data as well as the fluxes are included in Annex H, Table H-1.

The synthetic solution, Watt's bath and sulphamate bath rinse solutions follow nearly the same curvature. Within the time frame of the experiment, the nickel(II) concentration decreased without any problems below the PARCOM value for the synthetic solution, the Watt's bath and the sulphamate bath. Only the electroless nickel bath showed slower kinetics.

A possible explanation for the different behaviour of the electroless nickel bath rinse solution towards the others is that some of the additives of the electroless nickel bath rinse solution form complexes with nickel(II) which prevent a smooth transport of nickel(II) towards the organic phase.

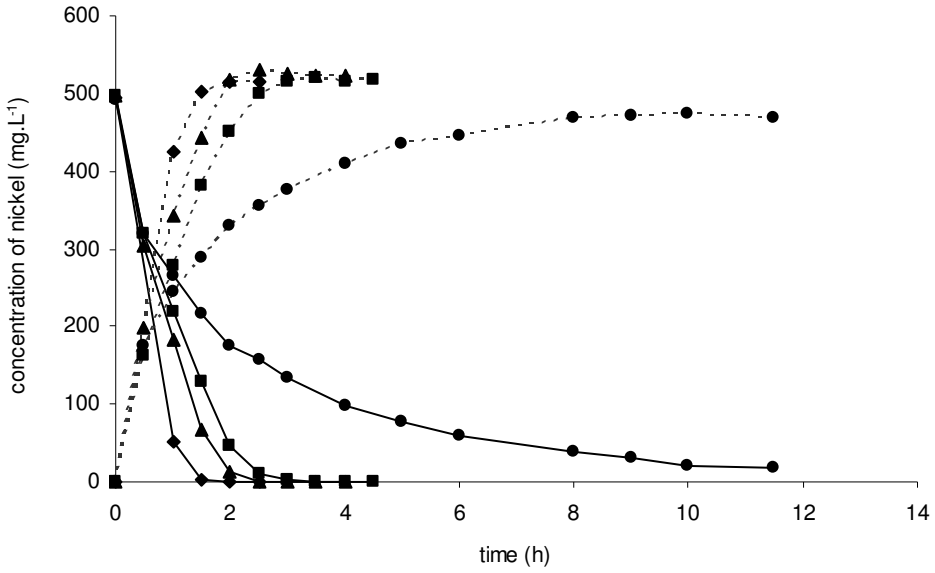

Figure 5-14. Experimental runs with real effluents:

(♦) synthetic feed solution; (■) Watt's bath; (▲) Sulphamate bath; (●) Electroless bath

—: feed concentration ; ---: strip concentration

5.4. INVESTIGATION OF THE STABILITY OF THE MEMBRANE – AGEING TEST

A flux or permeation decrease of the transported species can give an indication of membrane instability. Therefore, the stability of a membrane composed of 0.4 mol.L^{-1} LIX 860-I and 0.4 mol.L^{-1} CYANEX 302 was investigated by following the evolution of the flux. The results are represented in Figure 5-15. Measurement data are included in Annex H, Table H-2.

The same experimental device was used as depicted in Figure 5-11. An effluent stream containing 8.50 x 10^{-3} mol.L^{-1} (500 mg.L^{-1}) Ni(II) was used for the experimental work (volume = 8 L) (recirculation experiment). This effluent stream was simulated by diluting a Watt's bath. A volume of 3 L sulfuric acid (1.5 mol.L^{-1}) was used as strip solution. The nickel concentration was kept constant by pumping continuously Watt's bath to the feed solution. The pH was also kept constant at pH 4.5 by adding NaOH (pH control). The effective surface area of the membrane used in this experiment was 1.7 m^2 (Celgard 5PCM-104). Prior to the starting up of the analysis, the module was also circulated with feed and strip solution during two hours, followed by a replacement of the feed and strip solution by a new solution.

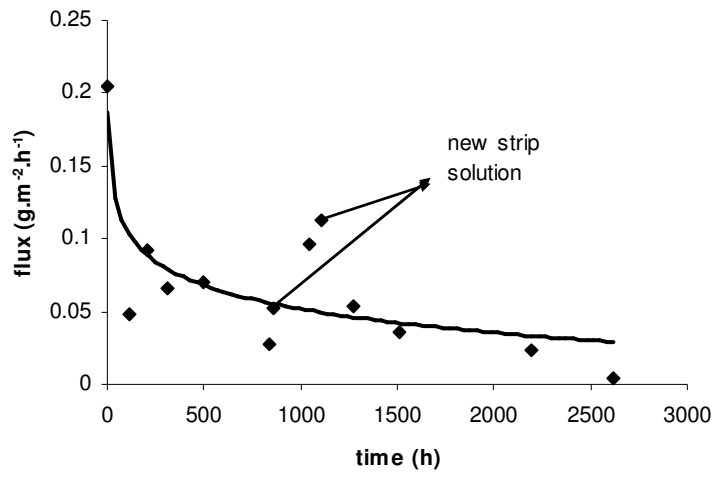

Figure 5-15. Investigation of the stability of the Celgard membrane impregnated with a mixture of LIX 860-I and CYANEX 302: flux as a function of time.

After 840 hours, the strip solution contained 0.4 mol.L^{-1} Ni(II) (or approximately 25 g. L^{-1}) and was replaced by a fresh solution of 1.5 mol.L^{-1} sulfuric acid. The strip solution was changed a second time after 1044 hours. Figure 5-15 shows that the flux gradually declines. However, two effects have to be taken into account. The flux decreases due to the ageing of the membrane, but also because the nickel(II) concentration in the strip phase became too high after a while. Replacement of the strip solution improved the flux. However, the high flux at the start of the process was not achieved anymore.

The major reason for a Supported Liquid Membrane to become instable is the loss of the liquid membrane (extractant and/or solvent) out of the pores of the support [5_16]. This loss of extractant can be due to several factors as mentioned in paragraph 2.7. One of the methods to enhance the SLM-lifetime is the reimpregnation of the support with the liquid membrane phase to keep the flux at a constant level as discussed extensively in paragraph 2.7.

5.5. CONCLUSION

This Chapter discussed the recovery of nickel(II) ions with the Supported Liquid Membrane technology. In a general study, the transport of nickel(II) has been compared to the transport behaviour of an alkaline earth metal ion, viz. magnesium(II). Secondly, experiments were performed on effluents streams created by the metal finishing industry to prove that the PARCOM level of nickel(II) (e.g. 0.5 mg.L^{-1}) can be reached with a Supported Liquid Membrane.

Liquid-liquid extractions indicated that the commercial available extractants exhibit rather limited extraction efficiencies for nickel(II). However, synergistic effects have been observed if mixtures of organophosphorous acid extractants and hydroxyoximes were applied as organic extractant solution. In the presence of the organophosphoric acid D2EHPA in the extractant mixture, high distribution coefficients were achieved, although this type of carrier shows only a limited selectivity against alkaline earth metal ions. A better selectivity was reached with an organophosphinic acid extractant, such as CYANEX 272 and CYANEX 302. However, distribution coefficients comparable with D2EHPA were not reached. If different types of hydroxyoximes are considered, the aldoximes (LIX 860-I) showed slightly higher extraction efficiencies compared to the ketoximes (LIX 84-I) when combined with an organophosphorous extraction reagent.

SLM experiments were carried out with flat membranes as well as with hollow fiber modules. The results with SLM confirmed the earlier obtained conclusions of the

liquid-liquid extraction experiments. Furthermore, the nickel(II) flux can be improved by increasing the carrier concentration. A maximum nickel(II) flux was obtained at a carrier concentration around 0.6 $mol.L^{-1}$. At higher extractant concentrations, effects of steric hindrance and/or an increase of the viscosity of the liquid film can inhibit the transport process. Increasing the acidity of the strip solution (1.5 $mol.L^{-1}$ versus 3 $mol.L^{-1}$ sulfuric acid) did not improve the nickel(II) flux.

In a second study, experiments were performed with real effluent streams. The experiments showed that with a mixture of 0.04 $mol.L^{-1}$ LIX 860-I and 0.04 $mol.L^{-1}$ CYANEX 302 diluted in kerosene, nickel(II) can be recovered out of industrial effluents below the PARCOM value of 0.5 $mg.L^{-1}$. Furthermore, the stability of the liquid membrane was checked during 2600 hours. Fluxes can be achieved of 0.05 – 0.1 $g.m^{-2}.h^{-1}$ for the first 1500 hours. However, a gradual decline of the nickel(II) flux was observed. The major reason for instability of a Supported Liquid Membrane is the loss of the liquid membrane (extractant and/or solvent) out of the pores of the support.

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Chapter 6

INTRODUCTION OF THE POTENTIAL ABILITIES OF POLYMER INCLUSION MEMBRANES AND IMMOBILIZED LIQUID MEMBRANES AS INNOVATIVE TECHNOLOGIES FOR THE REMOVAL OF METAL IONS

Several methods are described in literature to improve the stability of a Supported Liquid Membrane. These methods vary from small changes in the configuration of the Supported Liquid Membrane technology to novel types of liquid membranes [6_1]. Two of these novel types of liquid membranes are Polymer Inclusion Membranes (PIM) [6_2-6_6] and Immobilized Liquid Membranes (ILM) or fixed-site carrier membranes [6_7-6_9] (see also paragraph 2.7). The aim of these novel membrane types is not only to improve the stability of the membrane but also to maximize the membrane fluxes and to maintain the extraction efficiency and selectivity of the corresponding Supported Liquid Membrane system [6_2].

Polymer Inclusion Membranes are formed by casting a solution containing an extractant, a plasticizer and a base polymer such as cellulose triacetate (CTA) or polyvinylchloride (PVC) to form a thin, flexible and stable film [6_2-6_6]. The resulting self-supporting membrane can be used to separate metal ions in a similar way as in SLM. Both SLM and PIM involve the selective transport of a target species from one aqueous solution to another by means of the membrane. However, because the composition and morphology of PIM membranes are distinctively different from SLM, the actual bulk diffusion mechanisms within the membrane can be quite different [6_2-6_3]. Since the carrier is not covalently bound to the base polymer, it may be assumed that the actual diffusion mechanism in PIM membranes is intermediate between mobile carrier diffusion and fixed-site jumping [6_2-6_3]. It is also worth mentioning that PIM membranes have been used for more than 30 years in the form of polymer membrane ion-selective electrodes (ISEs) [6_2]. In sensing, fast ion exchange or metal ion complexation is required at the sample solution/membrane interface in order to establish a fast interfacial electrical potential difference while only negligible

transport of the metal containing species through the membrane within the timeframe of the measurement is allowed. For separation purposes, fast interfacial reactions are required but also high diffusion coefficients of the metal containing species within the membrane are desirable in order to achieve mass transport from the source to the receiving phase within a reasonable timeframe [6_2].

In SLM, the capillary force or interfacial tension is responsible for the bonding of the membrane liquid phase to the supporting pores. For PIM membranes, it is most likely that carrier, plasticizer and base membrane skeleton are bound to one another by some secondary bondings such as hydrophobic, van der Waals or hydrogen bonds [6_2-6_3]. These secondary bonds are much stronger than interfacial tension or capillary forces and can only be favourable in view of a long-term stability [6_2-6_3].

The second novel membrane type, Immobilized or fixed-site carrier membranes, implies the covalent attachment of the carriers or extractants onto the polymer backbone. The fixed-site jumping mechanism was proposed to describe the facilitated transport process in a solid membrane since the mobility of the carrier is restricted due to the covalent attachment of the carriers onto the polymer [6_2, 6_7]. For membranes with immobilized carriers, the extractant concentration must be sufficiently high in order to form a continuous chain across the membrane. Only then, an efficient transport of the solutes of interest can be assured. It must also be taken into account that fluxes are still rather restricted in solid membranes compared to liquid membranes [6_2, 6_7].

In this Chapter, preliminary studies are provided on Polymer Inclusion and Immobilized Liquid Membranes.

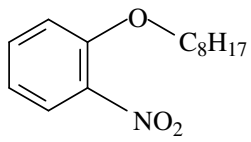
6.1. POLYMER INCLUSION MEMBRANES (PIM)

The three basic components of a Polymer Inclusion Membrane are the polymer, the carrier and the plasticizer.

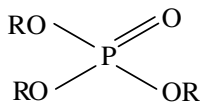
The polymers used for the formation of a PIM membrane are thermoplastic. They consist of linear polymer strands and because of the absence of cross-links between these strands, they can be dissolved in a suitable organic solvent [6_2]. Polyvinylchloride (PVC) and cellulose triacetate (CTA) have been the only two major polymers used for most of the PIM investigations conducted so far [6_2-6_6]. This is because both PVC and CTA can be used to prepare a thin film with a relatively simple procedure based on its dissolution in an organic solvent. Although both PVC and CTA have been widely used to prepare PIM

membranes, the effect of the properties of these polymers on the performance of PIM membranes is not clear yet [6_2-6_6].

While the base polymers merely provide mechanical support to the membrane, their bulk properties are an important factor in governing metal ion transport. The glass transition temperature (T_g) is often used to characterize the polymer flexibility. Below the glass transition temperature, the polymer is rigid [6_2]. Plasticizers are often added to the polymer to lower its T_g value and to create more flexible and less brittle membranes. All PIM membranes reported in literature contain some kind of plasticizer unless the carrier can also act as a plasticizer [6_2-6_6]. Plasticizers are generally organic compounds containing a hydrophobic alkyl backbone with one or several highly solvating polar groups [6_2-6_6]. The role of the plasticizer is to penetrate between polymer molecules and to "neutralize" the polar groups of the polymer with its own polar groups or to merely increase the distance between the polymer molecules and reduce the strength of the intermolecular forces [6_2-6_6]. As plasticizer, 2-nitrophenyloctylether (NPOE) and tri(2-n-butoxyethyl)-phosphate (TBEP) have been used in most PIM studies (see Figure 6-1) [6_2-6_6]. It is also noteworthy that several carriers such as quaternary ammonium salts and phosphoric acid esters can also play the role of a plasticizer. Consequently, no additional plasticizers are then necessary [6_2-6_6].



2-nitrophenyloctylether



R= - $(CH_2)_2O(CH_2)_3CH_3$

tri(2-n-butoxyethyl)phosphate

Figure 6-1. 2-nitrophenyloctylether (NPOE) and tri(2-n-butoxyethyl) phosphate (TBEP)

As carriers, acidic and chelating as well as neutral or solvating and macrocyclic carriers can be applied in PIM membranes (see also paragraph 2.2). Most research [6_2-6_3, 6_5-6_6] made use of Aliquat 336 as extraction agent. Another study [6_4] investigated LIX 84-I as extraction reagent in a PIM system. Cellulose triacetate was used as support and

tri(2-butoxyethyl)phosphate was used as plasticizer [6_4]. By using additives, e.g. ethanol, the solubility of the polymer improved as well as the copper(II) flux [6_4].

The usefulness of LIX 860-I in a PIM membrane for the recovery of copper(II) has not yet been studied. Therefore, the main goal of the work carried out on Polymer Inclusion Membranes is to develop a novel system which utilizes LIX 860-I as extractant in a PIM membrane for the recuperation of copper(II) and to evaluate its potential abilities compared to Supported Liquid Membranes. The influence of the total mass of the PIM membrane on copper(II) transport is discussed as well as the influence of the carrier and plasticizer concentration. But first of all, the general preparation and procedure is described.

6.1.1. General preparation and procedure

The membranes were prepared by dissolving an amount of a high molecular weight PVC (Selectophore – Fluka), plasticizer and carrier LIX 860-I in 10 mL solvent. The solution of PVC, plasticizer and carrier was stirred until a homogeneous solution was obtained. Then, the mixture was poured out into a Petri-dish with a diameter of 5 cm and the solvent was evaporated over night. The next day, the PIM membrane was peeled off from the Petri-dish and was clamped between the feed and strip compartment. In Figure 2-24, the two-compartment cell and its cross-section are depicted (effective membrane surface area of 0.00057 m^2). The same experimental device was used as shown in Figure 5-8 for the Supported Liquid Membrane processes with a flat membrane.

Tetrahydrofurane (THF) showed good characteristics as solvent for PVC. In dichloromethane or chloroform, the polymer often dissolved incompletely or not at all. Accordingly, THF was chosen as solvent. As far as the plasticizer is concerned, tri(2-butoxyethyl)phosphate (TBEP, Across Organics) showed the best characteristics in membrane preparation. With 2-nitrophenyl octyl ether (NPOE, Across Organics), the membranes were too elastic.

The experiment was set up by pumping feed (0.1 L) and strip (0.1 L) in the same direction along the PIM membrane (recirculation). The pumps were controlled at a flow rate of 0.5 $L.h^{-1}$. The feed containing 7.80 x 10^{-3} $mol.L^{-1}$ (or 500 $mg.L^{-1}$) copper(II) (pH 5.0) was prepared with the appropriate sulfate salt. As strip solution, 3 $mol.L^{-1}$ H_2SO_4 was used.

The copper concentrations in the aqueous phases were measured by Atomic Absorption after appropriate dilution. Fluxes of copper(II) are calculated at both the feed and strip side according to Equation (2-34). In general, only the fluxes calculated at the strip side

are displayed in the Figures, unless when differences occur between the fluxes calculated at the feed and strip side.

6.1.2. Determination of the copper(II) flux with SLM – flat membrane

In order to compare the effectiveness of a PIM configuration, a comparative study was made with a flat SLM membrane. A polypropylene micro-porous membrane, Celgard 2500, with an effective surface area of 0.00057 m^2, was applied in the same two-compartment cell as described above. The only difference in the experimental procedure is located in the membrane preparation. The Celgard membrane was impregnated with a solution of 0.2 $mol.L^{-1}$ LIX 860-I over night. Afterwards, the membrane was rinsed with deionised water to remove any excess of extraction reagent. Then, the flat membrane was clamped between the feed and strip compartment.

Figure 6-2 displays the fluxes calculated at the strip side as a function of the feed concentration. The measurement data as well as the fluxes are included in Annex I, Table I-1.

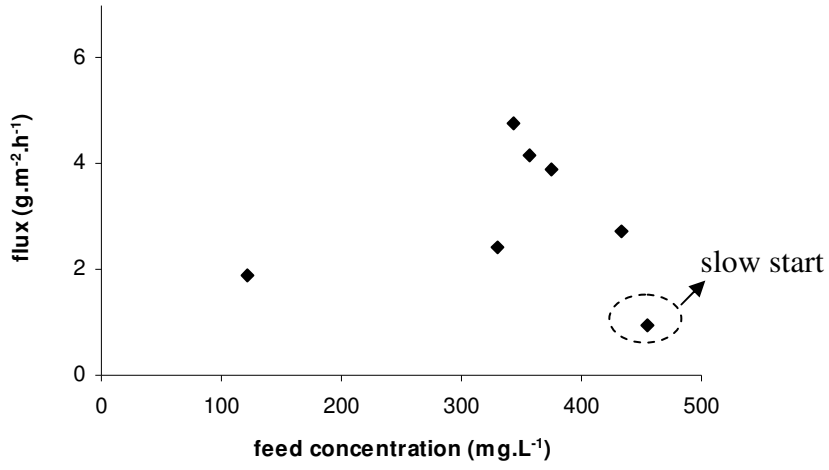


Figure 6-2. Determination of the copper(II) flux with SLM

The process started rather slowly (see Figure 6-2). This is contradictory to the fact that at the beginning of the experiment, the organic membrane was not loaded with metal ions, thus inferring a high metal uptake at the beginning. These lower fluxes were however noticed at both the feed and the strip side and show a rather difficult start of the process.

An average flux (strip side) of 3.3 $g.m^{-2}.h^{-1}$ was found for copper(II) during the SLM experiment with the flat membrane Celgard 2500. In fact, LIX 860-I is known as an excellent extractant for copper(II) [6_10]. In the succeeding paragraphs, the usefulness of LIX 860-I as extraction reagent for copper(II) in a PIM membrane will be discussed.

6.1.3. Influence of the carrier concentration on the transport of copper(II)

In this paragraph, the influence of the carrier concentration of the PIM membrane will be discussed. The membrane composition is always expressed as %w/w polymer/carrier/plasticizer. A total PIM mass of 600 mg was used during the membrane preparation. The plasticizer concentration was kept constant at 20 %w/w and the carrier concentration was varied between 30 and 50 %w/w. Accordingly, increasing the carrier concentration led to a decrease of the polymer concentration.

A lower initial feed concentration of 1.60 x 10^{-3} $mol.L^{-1}$ Cu(II) (or 100 $mg.L^{-1}$) was used for the PIM experiments in order to determine the differences in concentrations more accurately.

The fluxes of copper(II) calculated at the strip side are shown in Figure 6-3 and the experimental data are included in Annex I, Table I-2.

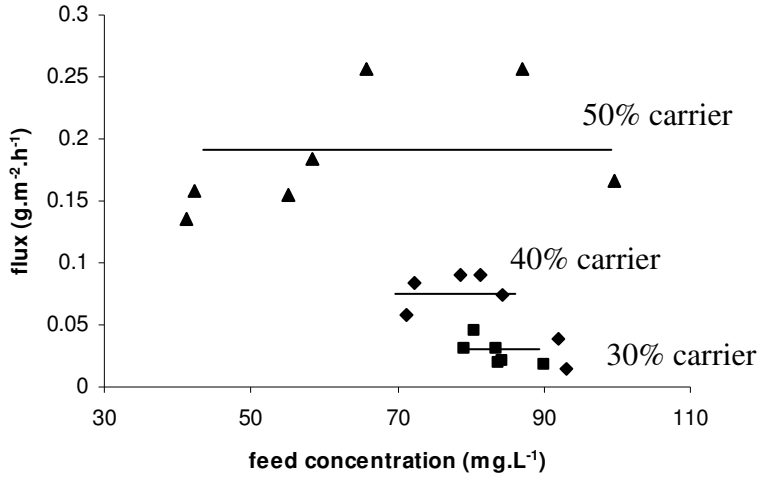


Figure 6-3. Influence of the carrier concentration on the copper(II) flux:
(■) 50/30/20, (♦) 40/40/20, (▲) 30/50/20
PVC/LIX 860-I/TBEP membrane (600 mg)

Increasing the carrier concentration improved the transport of copper(II). A membrane of 30/50/20 %w/w polymer/carrier/plasticizer showed the highest fluxes, although the fluxes obtained with SLM (Figure 6-2) were not reached yet. A further increase of the carrier concentration did not result in a successful membrane preparation. An increase of the carrier concentration affects the concentration of polymer or plasticizer if the same total weight of the membrane is maintained.

In literature [6_2-6_3], it was mentioned that the plasticizer also needs a minimal concentration in order to achieve reasonable metal fluxes as well as a satisfactory membrane softness and flexibility. The influence of the plasticizer concentration is discussed in the next paragraph.

6.1.4. Influence of the plasticizer concentration on the transport of copper(II)

A low plasticizer concentration is undesirable since it may cause the membrane to become more rigid and brittle due to a phenomenon referred to as the "anti-plasticizing" effect [6_2]. In literature [6_2], it was mentioned that the plasticizer concentration must be above a minimal level. In the case of PVC, this level is often found at 20 %w/w [6_2]. Furthermore, it was shown that the presence of a plasticizer also influences the permeability. PIM membranes made of the polymer CTA and Aliquat 336 as extractant but without plasticizer had a reduced permeability which represented about 4% of the permeability measured for membranes with plasticizer [6_3]. As the plasticizer concentration increased, the permeability increased until a limiting value was reached [6_3]. However, the plasticizer concentration may vary widely depending on both the plasticizer and the base polymer [6_2-6_3].

Within this research, the plasticizer concentration was varied between 10 and 30 % w/w and the carrier concentration was kept constant at 40 %w/w. A total PIM mass of 600 mg was used for the membrane preparation. The corresponding results are shown in Figure 6-4 (fluxes calculated at the strip side) and the experimental data are included in Annex I, Table I-3.

Figure 6-4 shows that when the plasticizer is present with a concentration of 10%, a very restricted flux was obtained. Increasing the plasticizer concentration to 20-30% w/w improved the flux. If a plasticizer concentration of 20 or 30% w/w is optimal is unclear since the fluxes calculated at the feed and strip side are contradictory. When the fluxes calculated at the strip side are considered, the highest fluxes were reached with a 40/40/20 %w/w

membrane. Based on the fluxes calculated at the feed side, higher fluxes were achieved with a 30/40/30 % w/w membrane compared to the 40/40/20 %w/w membrane (see also Annex I, Table I-3). This is also shown in Figure 6-5 which displays the copper(II) concentrations in the feed and strip solution as a function of time.

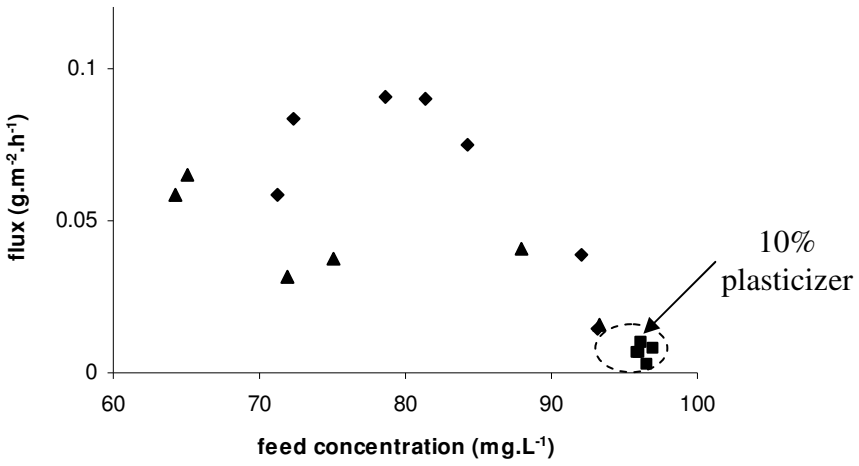


Figure 6-4. Influence of the plasticizer concentration on the copper(II) flux:
(■) 50/40/10, (♦) 40/40/20, (▲) 30/40/30
PVC/LIX 860-I/TBEP membrane (600 mg)

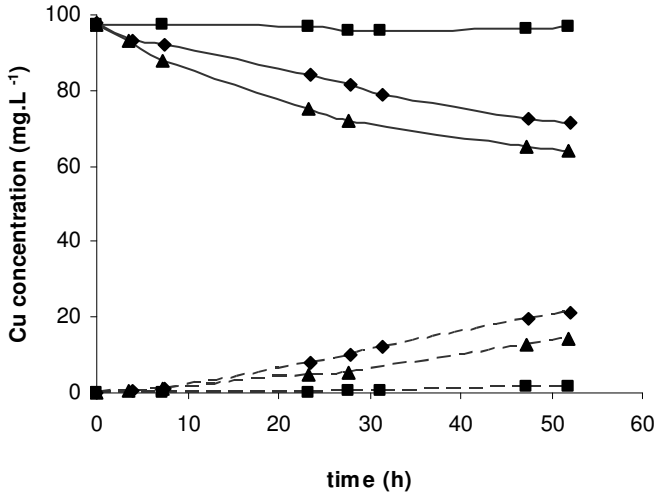


Figure 6-5. Concentration of copper(II) in the feed (–) and
the strip solution (-----) as a function of time:
(■) 50/40/10, (♦) 40/40/20, (▲) 30/40/30
PVC/LIX 860-I/TBEP membrane (600 mg)

It seems that when the plasticizer is present with a concentration of 30%, the stripping process becomes more difficult. In literature [6_2], it was mentioned that an excessive plasticizer concentration is problematic because the excess plasticizer is able to migrate to the membrane/aqueous interface and form a film on the membrane surface, which could create an additional barrier to the transport of the metal ions across the membrane. This may explain the difficult decomplexation that was noticed at the strip side with the 30/40/30 %w/w membrane. However, the extraction of copper(II) at the feed/membrane interface encountered no difficulties.

6.1.5. Influence of the total mass of the PIM membrane on the transport of copper(II)

PIM membranes of a different total mass, ranging from 800 till 400 mg, were prepared in order to evaluate its corresponding influence on the transport behaviour of copper(II). By decreasing the total PIM mass (surface area is kept constant), the thickness of the membrane is reduced, which can only be beneficial to the metal ion transport. The same membrane composition was used for the different membranes, namely 40/40/20 %w/w of polymer/carrier/plasticizer. The results are depicted in Figure 6-6 and the experimental data are included in Annex I, Table I-4.

In Figure 6-6, the fluxes calculated at the strip side are displayed. However, it must be noticed that at the beginning of the experiments, especially in the case of the 800 and 600 mg membranes, a very low flux was achieved at the strip side whereas this was not the case for the fluxes calculated at the feed side (see also Annex I, Table I-4). This induction period was less pronounced for the thinner membranes.

In general, the membrane of 400 mg showed a trend towards higher copper(II) fluxes. With thicker membranes, especially the 800 mg membrane, the stripping process encountered some difficulties (see also Annex I, Table I-4). A lower PIM mass resulted into a thinner membrane, which can only be beneficial for the metal ion transport. Nevertheless, a compromise must be found between the thickness of the membrane and its mechanical properties. Furthermore, the fluxes fluctuated around 0.10 $g.m^{-2}.h^{-1}$ for the 400 mg membrane, which is at least one order of magnitude lower compared to the SLM-experiment of paragraph 6.1.2 (3.3 $g.m^{-2}.h^{-1}$).

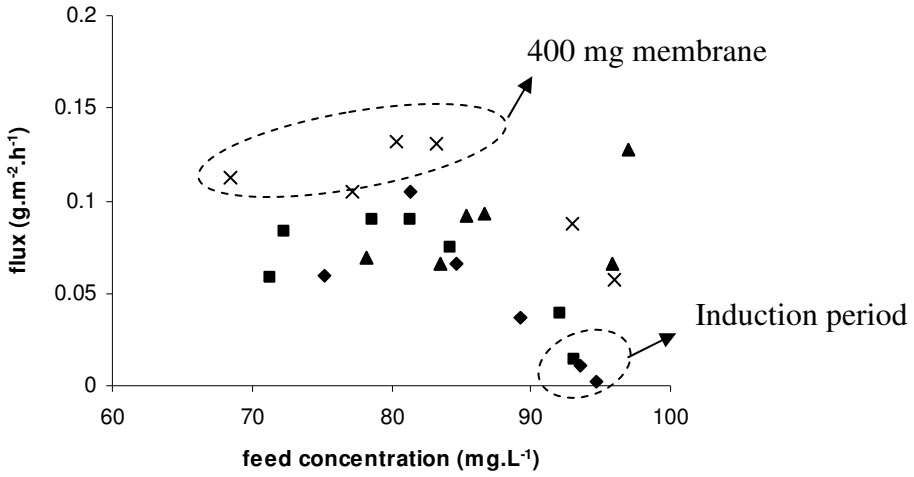


Figure 6-6. Influence of the total mass of the PIM membrane on the copper(II) flux (♦) 800 mg, (■) 600 mg, (▲) 500 mg, (×) 400 mg

6.1.6. Conclusion about Polymer Inclusion Membranes

In this Chapter, a preliminary study was made to gain a first insight in the capabilities of the Polymer Inclusion Membrane technique. The extraction efficiency of copper(II) with LIX 860-I in Polymer Inclusion Membranes has been compared to the corresponding Supported Liquid Membrane system.

This preliminary study tried to make a first evaluation on the role of the three basic components of a PIM membrane, viz. polymer, plasticizer and carrier. Polyvinylchloride was chosen as polymer. As plasticizer, tri(2-butoxyethyl)phosphate showed the best characteristics in membrane preparation compared to 2-nitrophenyl octyl ether. Different solvents were tested for the membrane casting. Only tetrahydrofurane was capable to dissolve the mixture of the different components.

Increasing the carrier concentration (30 till 50%) led to enhanced extraction rates, although only limited increments of the carrier concentration are possible in view of the mechanical properties. An increase of the carrier concentration leads to a decrease of polymer or plasticizer concentration if the same total weight of the membrane is maintained. In addition, a minimal plasticizer concentration is necessary to increase the membrane softness and flexibility but also for an increased metal permeability. With a plasticizer concentration of 10%, nearly no copper(II) transport was obtained. At a plasticizer concentration of 30%,

the stripping process became more difficult. Considering the total PIM mass, the membrane of 400 mg showed a trend towards higher copper(II) fluxes. Reducing the total mass of the membrane resulted into a thinner membrane and can only be favourable for the metal transport.

This preliminary research also indicated rather limited copper(II) fluxes with PIM membranes compared to these obtained with Supported Liquid Membranes. The PIM-fluxes were at least one order of magnitude lower compared to SLM-fluxes. Therefore, it seems very doubtful that these PIM systems will be able to replace SLM systems in the near future.

6.2. IMMOBILIZED LIQUID MEMBRANES (ILM) OR FIXED-SITE CARRIER MEMBRANES

A second mode of improving the stability of a Supported Liquid Membrane is the covalent attachment of the carrier or extractant molecules onto the polymer backbone, resulting in no loss of carrier or solvent. These membranes are often called Immobilized Liquid Membranes (ILM) or fixed-site carrier membranes or coordination polymers [6_7-6_9]. The challenge is the development of a system which contains the correct reactive groups to provide chemical specificity for one component in the feed solution [6_7].

Within this paragraph, preliminary research is provided in order to gain a first insight in the effectiveness of this second novel membrane type. In ILM, a different transport mechanism is involved compared to Supported Liquid Membranes. In a solid membrane, a "fixed-site jumping" mechanism is used to describe the facilitated transport process in a solid membrane [6_2, 6_7]. This jumping mechanism requires a sufficiently high carrier concentration so that a continuous chain across the membrane can be formed [6_7].

In order to anchor the correct reactive groups onto the polymer matrix, the polymer must provide functional groups for modification. Functional polymers represent an important class of polymeric materials. Their synthesis is usually carried out by means of classical methods such as polymerisation or polycondensation of functional monomers as well as by the chemical modification of the polymer [6_8]. The chemical modification method is the most frequently used procedure.

The aim of this novel research is to modify a commercial available polymer membrane with a chelating extractant, viz. LIX 860-I or 8-hydroxyquinoline. This modified polymer membrane replaces the micro-porous polymer membrane impregnated with extractant solution (= "Supported Liquid Membrane"). In SLM-applications, a polypropylene

micro-porous polymer membrane is most frequently used [6_10-6_11]. However, these polypropylene membranes do not possess functional groups available for modification. With plasma treatment (NH_3, N_2/H_2, O_2), nitrogen- and/or oxygen-containing polar groups can be created on the membrane surface [6_12]. However, a complete modification of the polymer membrane is necessary to guarantee the metal ion transport towards the strip phase. Therefore, other available functional polymers were screened. Besides the availability of functional groups for modification, the membrane must fulfil some additional requirements for the metal transport through the Immobilized Liquid Membrane. Hydrophobic functional polymer membranes are required with a limited thickness; otherwise the thickness will inhibit the metal transport.

Most of the research has been done with an ethylenetetrafluoroethylene (ETFE) membrane (thickness of 50 µm), which had been grafted with vinylbenzylchloride (Solvay) (65% grafting degree) and a polysulfone membrane, Desal E-500 (Desalination Systems). The ETFE membrane has been chosen because of its hydrophobicity and the presence of chloride functional groups which opens perspectives for modification routes. Secondly, the polysulfone membrane Desal E-500 was chosen because of the various modification routes available in literature [6_13-6_15]. Furthermore, this membrane showed satisfactory transport properties for nickel(II) during SLM [6_10].

A discussion of the modification of both membranes and the corresponding results are given in the succeeding paragraphs.

6.2.1. Ethylenetetrafluoroethylene (ETFE) membrane

The presence of the chloride functional group through grafting of the ETFE membrane with vinylbenzylchloride makes it possible to provide the polymer membrane with amine functional groups, which can then be used for the anchoring of the extractant molecules as shown in Figure 6-7.

The first step of the modification procedure of the ETFE membrane consisted of the formation of primary amine functional groups onto the polymer membrane through treatment of the membranes with liquid ammonia at high temperature and high pressure (see step 1 of Figure 6-7) [2_16-2_17]. The membranes were treated during 48 hours with liquid ammonia at 50°C (30 bar) and at 100°C (60 bar). Elemental analysis (nitrogen) of the membranes showed a substitution degree of approximately 60% of the available chloride functional groups (2 mmol Cl^- / g membrane) into amine groups at both temperatures.

The second step of the modification process (step 2 of Figure 6-7, not described in literature) consisted of introducing an extractant molecule onto the polymer membrane. 2-Hydroxybenzaldehyde (or salicylaldehyde) was chosen as reagent in order to create specific sites onto the polymer matrix which resemble to the structure of 5-dodecylsalicylaldoxime or LIX 860-I, an excellent extraction reagent for copper(II).

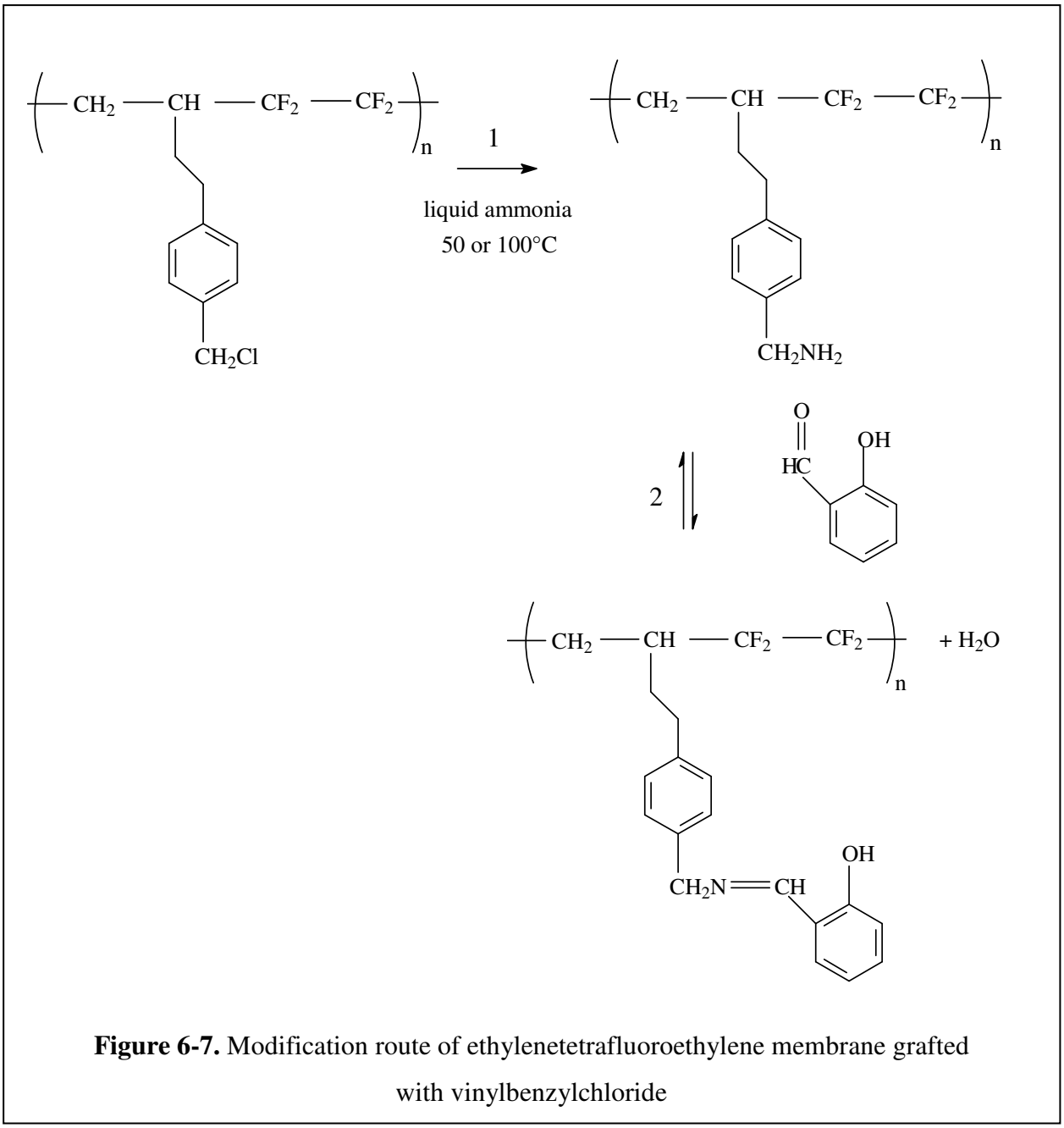


Figure 6-7. Modification route of ethylenetetrafluoroethylene membrane grafted with vinylbenzylchloride

These reactions were carried out by refluxing the membrane (± 0.2 g) and 0.5 g (4 mmol) salicylaldehyde in 50 mL absolute ethanol during 7 hours. Molecular sieves were added to shift the equilibrium of the reaction into the direction of the anchored polymer membrane.

The brominated salicylaldehyde (0.8 g, 4 mmol) (see Figure 6-8) was used in order to identify if the reaction was successful or not through determination of the bromine concentration of the modified membrane with capillary electrophoresis (after preceding destruction).

If the amount of bromine functions onto the polymer membrane at the end of the modification route is compared to the initial available chloride functional groups (= 2 mmol Cl^- / g membrane), a conversion degree of 20% was obtained.

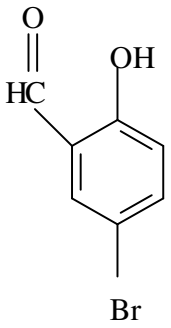


Figure 6-8. Structure of 5-bromo-2-hydroxybenzaldehyde

The final step consisted of testing the extraction of copper(II) with the modified ETFE membrane (modified with 5-bromo-2-hydroxybenzaldehyde) in a SLM-shaking experiment. The experimental device is shown in Figure 6-9.

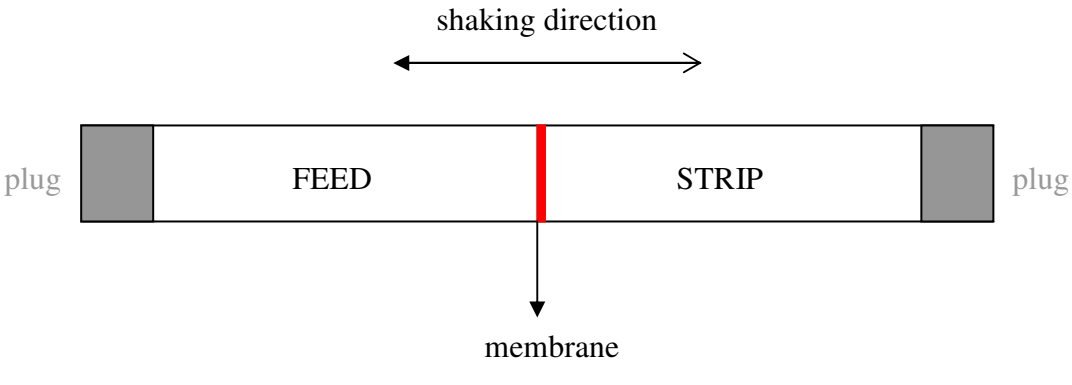


Figure 6-9. Experimental device for SLM-shaking experiment

The feed (0.03 L) containing 7.80 x 10^{-3} mol.L^{-1} (or 500 mg.L^{-1}) copper(II) (pH 4.0) was prepared with the appropriate sulfate salt. As strip solution, 3 mol.L^{-1} H_2SO_4 (0.03 L) was used. The membrane had an effective surface area of 0.00038 m^2. Each hour, the copper(II) concentration was measured in the feed and the strip solution with Atomic Absorption.

However, only 0.7 mg.L^{-1} Cu was detected in the strip solution after 24 hours with the modified membrane. The same experiment was also repeated with a non-modified ETFE membrane that was impregnated with a LIX 860-I solution (7 vol% in kerosene Shellsol D100 - Shell Chemicals). After 24 hours, 3.7 mg.L^{-1} Cu was determined in the strip solution. For both experiments, the pH only decreased from 4.0 to 3.4 after 24 hours, suggesting that the thickness and/or porosity of the ETFE membrane and/or a too low density of active groups may have restricted the metal transport.

6.2.2. Polysulfone membrane

General methods of introducing functional groups into polysulfones involve a direct lithiation or a dual process of bromination/lithiation, as well as the amination of polysulfone by novel azide intermediates [6_9, 6_13-6_15]. These modifications make use of lithiated polymer intermediates which are reactive to a variety of electrophiles.

The reaction scheme applied for the modification of the polysulfone membrane, Desal E-500, is shown in Figure 6-10 [6_9, 6_13-6_14]. In literature, this modification route was successfully applied on polysulfone UDEL P3500 pellets [6_9, 6_13-6_14]. Afterwards, a membrane film was formed which was tested for the recovery of some metal ions, viz. copper(II) and nickel(II) [6_9]. 70% copper and 82% nickel were respectively recovered [6_9].

The first challenge of this research was to apply the modification procedure directly onto the Desal E-500 membrane. Afterwards, the modified membrane can be implemented in SLM without any further treatment. This means that both the configuration of the membrane and mechanical properties must be maintained during the reactions. This implies that the polymer cannot be dissolved during the modification reactions in contrast to the corresponding polymer powder or pellet form.

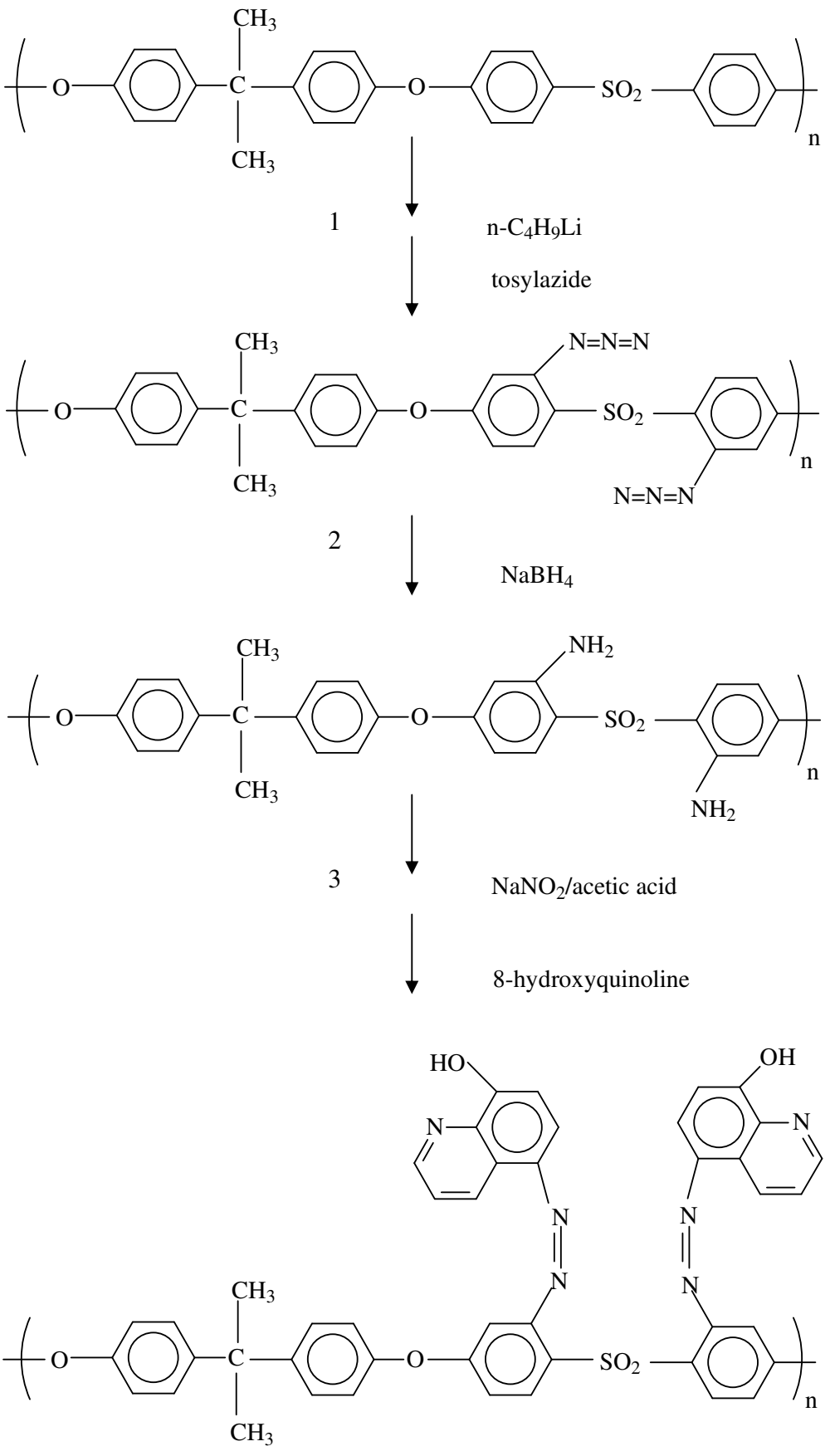


Figure 6-10. Chemical modification route of a polysulfone polymer [6_9, 6_13-6_14]

The chemical modification of polymer membranes showed more difficulties compared to its powder or pellet form. In fact, during modification of a polymer membrane, the selection of useful solvents is very limited in order to maintain the membrane characteristics. Furthermore, reactions have to be performed in heterogeneous mode which results in a slow diffusion of the reagents into the polymer matrix in contrast to the homogeneous reaction mixture of the powder form (dissolution of all reagents). This is shown and discussed by means of the modification of the polysulfone polymer, Desal E-500, with 8-hydroxyquinoline.

In literature [6_9, 6_13-6_14], the modification route used tetrahydrofurane (THF) as solvent for the modification of polysulfone UDEL P3500 (pellets). In the case of a polymer membrane, this solvent could not be applied because the membrane film was chemically not resistant against THF. Hexane did not affect the properties of the membrane. Therefore, hexane was used as reaction solvent for the modification of the Desal E-500 membrane. However, no indications were found of a successful modification of the polymer membrane with primary amino groups. Consequently, the modification method was tested out on polysulfone pellets, UDEL 1700 (Union Carbide) instead of the polymer membrane to evaluate the modification method described in literature [6_9, 6_13-6_14]. The general procedure is described in the next paragraph.

6.2.2.1. General procedure [6_9, 6_13-6_14]

Two general steps can be distinguished in the modification procedure. At first, the amination of the polysulfone polymer takes place (see step 1-2 of Figure 6-10). Secondly, a chelating extractant, viz. 8-hydroxyquinoline can be anchored onto the polysulfone matrix (see step 3 of Figure 6-10). Instead of 8-hydroxyquinoline, also another ligand can be anchored, viz. salicylaldehyde (see step 2 of modification route described in Figure 6-7).

In the succeeding paragraphs, the general procedure of the modification route of polysulfone with 8-hydroxyquinoline (see Figure 6-10) is discussed. The reagents were used in the same molar ratios as described in [6_9, 6_13-6_14].

Amination of polysulfone [6_9, 6_13-6_14]

The first step in the process is the formation of azide functional groups (step 1 of Figure 6-10), followed by its reduction with sodium borohydride into primary amino groups (step 2 of Figure 6-10). The reactions were carried out under argon atmosphere.

6.3 mmol of polysulfone (UDEL 1700) was dissolved in 50 mL distilled and dried tetrahydrofurane. The solution was cooled until -65 °C by means of acetone and nitrogen and 13.5 mmol (2.15 equivalents) n-butyllithium was injected into the reaction mixture, followed by 30 minutes stirring.

Afterwards, 18.8 mmol (3 equivalents) p-toluene-sulfonylazide (or tosyl azide, see Figure 6-11), dissolved in 3.8 mL tetrahydrofurane, was injected into the reaction mixture and the temperature was raised to -50 °C. A mixture ethanol:water (10:1) (62.5 mL) was added to the reaction mixture and the temperature was raised to 10 °C.

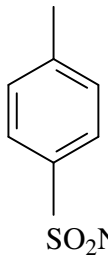


Figure 6-11. Structure of tosyl azide

The polymer suspension was cooled to 0 °C and 18.8 mmol (3 equivalents) $NaBH_4$ was added to the reaction mixture to reduce the azide functional groups. After ten minutes, the ice bath was removed and the reaction mixture was stirred over night.

FT-IR spectra and elemental nitrogen analysis of the polysulfone matrix were used to identify if the reaction had been successfully accomplished.

Attachment of a chelating agent onto the polymer matrix [6_9, 6_13-6_14]

The last step of the modification process involved the anchoring of 8-hydroxyquinoline onto the aminated polysulfone polymer (step 3 of Figure 6-10).

The aminated polysulfone powder (1 g) was soaked in a 0.2 $g.L^{-1}$ sodium nitrite and 0.1 $g.L^{-1}$ acetic acid aqueous solution (100 mL) for 1 hour at 0 °C, washed with cold water (100 mL), and then soaked in a 0.2 $g.L^{-1}$ ethanolic solution of 8-hydroxyquinoline (100 mL) for 1 hour at 0 °C, while stirring.

6.2.2.2. Results

The first step of the modification route involved the functionalisation of the polysulfone polymer with primary amino functions (step 1 and step 2 of Figure 6-10). FT-IR spectra were made of the polymer UDEL 1700 after step 2 of the modification route (see

Figure 6-10). The spectrum is displayed in Figure 6-11 and is compared to the polysulfone polymer without any pre-treatment.

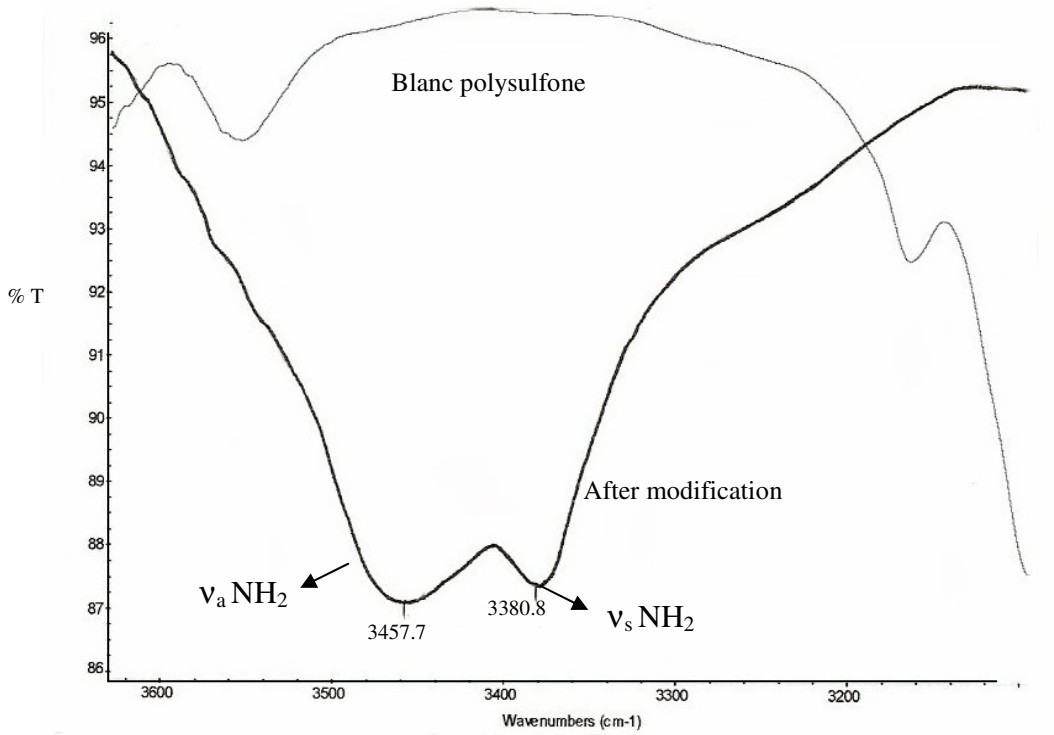


Figure 6-12. Comparison of FT-IR spectra of polysulfone UDEL 1700 without modiication and the corresponding spectrum after amination

The FT-IR spectra show a change in the wavenumber range of 3500-3300 cm^{-1}. The two bands appearing at 3457.7 and 3380.8 cm^{-1} represent the anti-symmetrical and symmetrical stretching vibrations of the primary amino groups, respectively. In addition, elemental analysis of the polymer matrix gave a more quantitative insight in the degree of modification. 1 g of modified polysulfone UDEL 1700 powder contained 3.8 mmol nitrogen (degree of substitution of polysulfone unit = 1.7). Thus, FT-IR as well as elemental analysis confirmed the successful modification of the polysulfone UDEL 1700 with primary amine functional groups in tetrahydrofurane as solvent, this in contradiction to the modification route which was applied onto the polymer membrane in hexane.

The next step in the modification procedure is the introduction of 8-hydroxyquinoline onto the polymer matrix (step 3 of Figure 6-10). Elemental analysis indicated however that 1 g of polysulfone UDEL 1700 powder (after modification step 3) contained 1.5 mmol

nitrogen, which is less than the result obtained after step 2 of the modification procedure (3.8 mmol nitrogen). After introduction of 8-hydroxyquinoline, the nitrogen content should however increase (see structure Figure 6-10). It must however be mentioned that the product obtained after step 2 of the modification procedure showed different colour intensities from slightly yellow to dark yellow. This indicated that the reaction did not proceed in a homogeneous way and can possible declare the lower nitrogen content after step 3 of the modification process.

Finally, the modified polysulfone powder was tested for the uptake of copper(II) ions in a batch experiment. 0.2 g powder was stirred in a beaker during 48 hours with 25 mL of a copper(II) solution (10 $mg.L^{-1}$, pH 5.2) prepared from the corresponding sulfate salt. A comparison was made with the polysulfone powder without any modification and the aminated polysulfone. The results are shown in Table 6-1.

Table 6-1. Batch experiments with modified and non-modified polysulfone polymer

Polymer	copper(II) concentration after 48 hours ($mg.L^{-1}$)	pH after 48 hours
Non-modified polysulfone	9.7	5.0
Aminated polysulfone	8.0	3.2
Modified polysulfone with 8-hydroxyquinoline	10	3.0

The results of Table 6-1 show that 1 g aminated polysulfone powder extracted 0.25 mg Cu(II). The modified polysulfone polymer with 8-hydroxyquinoline showed no extraction at all, although a decline of the pH was observed. In literature [6_9], extraction of copper(II) and nickel(II) was obtained with the modified polysulfone powder UDEL P3500. However, it must be mentioned that only concentrations in the order of $\mu g.L^{-1}$ were used (4 $\mu g.L^{-1}$ for copper(II) and 8 $\mu g.L^{-1}$ for nickel(II)) [6_9].

6.2.3. Conclusion about Immobilized Liquid Membranes

The aim of this novel research was to modify a commercial available polymer membrane with a chelating extractant, viz. LIX 860-I or 8-hydroxyquinoline. This modified polymer membrane may eventually replace the micro-porous polymer membrane impregnated with extractant solution in Supported Liquid Membrane applications. Preliminary research

was mainly focussed on the modification of an ethylenetetrafluoroethylene (ETFE) membrane grafted with vinylbenzylchloride (Solvay) and a polysulfone membrane, Desal E-500 (Desalination systems).

The first step of the modification procedure of the ETFE membrane consisted of the formation of primary amine functional groups onto the polymer membrane through treatment of the membranes with liquid ammonia at high temperature (and high pressure). A substitution degree of 60% of the initial chloride amount was obtained at 50°C (30 bar) and at 100°C (60 bar). Secondly, 5-bromo-2-hydroxybenzaldehyde was anchored onto the aminated ETFE membrane. Analysis of the bromine concentration of the membrane showed a substitution degree of 20% compared to the initial available chloride functional groups. A SLM-shaking experiment showed however nearly no copper(II) extraction. The thickness and/or porosity of the membrane and/or a too low density of active groups may have obstructed the metal transport.

In the case of the polysulfone membrane, Desal E-500, the first step of the modification procedure consisted of a direct lithiation, followed by the amination of the polysulfone by tosyl azide. The primary amine functional groups can then be used for further modification with chelating agents. It became soon clear that the direct modification of the polysulfone membrane was difficult to achieve due to the absence of a homogeneous reaction mixture and limitations concerning the solvent as well as a slow diffusion of the reagents into the polymer membrane. Therefore, the same modification route was applied onto polysulfone pellets, viz. UDEL 1700 of Union Carbide. FT-IR as well as elemental nitrogen analysis indicated a successful amination of the polysulfone UDEL 1700 (degree of substitution of polymer unit = 1.7). The second step of the modification procedure involved the anchoring of the extractant molecule, viz. 8-hydroxyquinoline, followed by batch extraction experiments on copper(II). The results showed that 1 g aminated polysulfone extracted 0.25 mg copper(II). The polysulfone membrane modified with 8-hydroxyquinoline showed however no copper(II) extraction.

6.3. CONCLUSION

In this Chapter, preliminary research was provided to gain a first insight in the potential abilities of two novel types of liquid membranes as techniques for the removal of metal ions from effluent streams, viz. Polymer Inclusion Membranes (PIM) and Immobilized Liquid Membranes (ILM) or fixed-site carrier membranes.

The primary goal of this research on Polymer Inclusion Membranes involved the development of a PIM membrane with LIX 860-I as extraction reagent for the extraction of copper(II). Polyvinylchloride was used as base polymer. As solvent, tetrahydrofurane showed the best characteristics for membrane preparation, while as plasticizer, tri(2-butoxyethyl)phosphate (TBEP), was chosen.

The influence of both carrier and plasticizer concentration was investigated as well as the influence of the total PIM mass on the transport rate of copper(II). Increasing the carrier concentration improved the extraction of copper(II), although only limited increments of the carrier concentration are possible in view of the mechanical properties of the membrane. The plasticizer concentration must be above a minimum level, otherwise the membrane becomes too rigid and the metal flux is hindered. On the other hand, at a high plasticizer concentration (30%), the stripping process became more difficult. Reducing the total mass of the membrane resulted into a thinner membrane which improved the metal ion transport. In general, fluxes in the range of 0.1-0.2 $g.m^{-2}.h^{-1}$ were reached for copper(II) with PIM membranes while a flux of 3 $g.m^{-2}.h^{-1}$ was obtained with a corresponding SLM system.

The second part of the research involved a first evaluation of the preparation and efficiency of an Immobilized Liquid Membrane as alternative for the impregnated membranes used in Supported Liquid Membrane systems. The chemical modification of two membranes was investigated: an ethylenetetrafluoroethylene membrane grafted with vinylbenzylchloride (Solvay) and the polysulfone membrane, Desal E-500 (Desalination Systems). The choice of reaction solvent is however rather limited in the case of Desal E-500 in order to maintain its membrane properties.

The modification route of the ETFE membrane grafted with vinylbenzylchloride involved the amination of the polymer membrane with liquid ammonia. A substitution degree of 60% of the available chloride functional groups was reached at 50°C and 100°C (30 and 60 bar, respectively). In a second step 5-bromo-2-hydroxybenzaldehyde was anchored onto the polymer backbone. A final substitution degree of 20% was obtained compared to the initial chloride functions available on the membrane for modification. SLM-batch experiments showed however a very restricted copper(II) transport. This was also the case with the corresponding impregnated ETFE membrane with LIX 860-I, suggesting that the thickness and/or porosity of the polymer membrane and/or a too low density of active groups restricted the copper(II) transport.

The modification route of the polysulfone membrane involved the direct lithiation of the membrane followed by its amination with tosyl azide and its subsequent reduction with sodium borohydride. After amination, the final anchoring of a chelating agent, 8-hydroxyquinoline, could be performed. The experimental work showed that the modification of a polymer membrane is much more difficult to achieve compared to the modification of the powder form and its subsequent formation of a membrane due to the absence of a homogeneous reaction mixture (dissolution of all reagents), slow diffusion of reagents in the polymer membrane for modification and the limited choice of solvent in order to maintain the membrane characteristics. In the case of polysulfone UDEL 1700 – the corresponding pellet form, FT-IR as well as elemental analysis showed a substitution degree of 1.7 of the polymer unit for the aminated polysulfone. After the final anchoring of 8-hydroxyquinoline, batch extraction experiments were performed to determine the extent of copper(II) extraction. 1 g of aminated polysulfone extracted 0.25 mg copper(II). The modified polysulfone with 8-hdyroxyquinoline showed no metal extraction.

On the basis of the preliminary research, a global view can be given on the effectiveness of Polymer Inclusion and Immobilized Liquid Membranes as alternative techniques for Supported Liquid Membranes. It seems very doubtful that fluxes in the same order of magnitude as for Supported Liquid Membranes will be reached. The first results obtained with PIM showed already that the fluxes were at least one order of magnitude lower compared to SLM. It is also expected that with Immobilized Liquid Membranes, the fluxes of SLM will not be reached due to the different transport mechanism involved, viz. the fixed-site jumping mechanism, which is expected in solid membranes. This implies a certain carrier concentration threshold in order to create a continuous chain across the membrane.

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Chapter 7

SUMMARY AND CONCLUSIONS

Heavy metal ions constitute a crucial part of most industrial processes. Consequently, heavy metal ions are present in different types of effluent streams resulting from the metal finishing industry, textile industry, mining industry and many other branches. These effluent streams are important sources of pollution because of their high toxicities and wide environmental spreading. Due to the very strict legislations concerning environmental regulation, the focus has shifted away from emission reduction through "end-of-pipe" treatment towards integrated approaches which are also aimed at the recycling of these metal ions. Recycling of metal ions has two major effects upon our society. The recovery of metal ions results in a decrease of the general pollution of the environment. Moreover, recycling also leads to the conservation of natural resources.

Due to the very strict legislations, new technologies are constantly emerging for treating and purifying all kinds of waste water. One of these innovative technologies is the Supported Liquid Membrane (SLM) technique. The "Supported Liquid Membrane" technology is a membrane-based solvent extraction method that uses a micro-porous hydrophobic membrane as supporting layer. This membrane is impregnated with an organic solvent containing the specific carrier molecules for metal ion extraction. At one side of the membrane the effluent stream (feed) is pumped. At the other side, an acid solution (strip) is circulated. At the feed/membrane interface, the complexation reaction takes place. The metal complex diffuses through the liquid membrane followed by a decomplexation of the metal complex at the membrane/strip interface. The metal ions are transported against their own concentration gradient due to the concentrated strip solution (driving force of protons). In this way, very dilute solutions can be treated very efficiently. Other important advantages of the SLM-technology are the lower amounts of extractants necessary compared to conventional solvent extraction methods and the possibility to combine the extraction and stripping process in a single unit operation.

The SLM technology has proven already its usefulness for the recuperation of copper ions from industrial effluents. For other metal ions such as nickel and cobalt, it is quite

difficult to achieve reasonable fluxes. A lot of research efforts have been made over the last two decades to understand the complexation mechanisms of the extraction processes. However, the extraction circumstances can vary a lot and complexation mechanisms are not always unequivocal. Therefore, the extractions of some metal complexes applicable in Supported Liquid Membranes were studied in depth in the present work. These studies were mainly focussed on the metal ions copper(II), nickel(II), cobalt(II), iron(III, II) and magnesium(II). As extractants, D2EHPA [di(2-ethylhexyl)phosphoric acid], CYANEX 272 [di(2,4,4-trimethylpentyl)phosphinic acid], CYANEX 302 (the monothioderivative of CYANEX 272), CYANEX 301 (the dithioderivative of CYANEX 272) and LIX 860-I [5-dodecylsalicylaldoxime] were investigated either separately or in combination with a second extractant molecule.

At first, the extraction performance of these extractants for the metal ions copper(II), nickel(II), cobalt(II), iron(III, II) and magnesium(II) was studied and compared to the application of mixed extractant systems. Hexane and 1-decanol were applied as diluents in order to determine the effect of the polarity of the diluent on the extraction efficiency of the metal ions and to investigate if changes occur in the configuration of the metal complexes. The FT-IR en UV-VIS absorption spectra of the organic phases were used for characterization of the metal complexes.

Different extraction efficiencies were found for some metal ions with an inert diluent compared with a chemically active one such as 1-decanol. For LIX 860-I, the extraction percentages of copper(II), iron(III), cobalt(II) and magnesium(II) decreased in 1-decanol compared to hexane. LIX 860-I is able to react with a diluent with electron-donor properties, such as ethanol or 1-decanol. These interactions of the diluent with the extractant molecules affect the activity of the extractant and change the extraction performance. On the other hand, also interactions between the diluent and the metal complex can occur. In the case of cobalt(II)-D2EHPA complexes for instance, the diluent-metal complex interactions led to a change in coordination geometry from a tetrahedral configuration in hexane towards an octahedral configuration in a more polar solvent.

The experiments with mixtures of extractants showed important synergistic effects for the extraction of nickel(II) with a mixture of LIX 860-I and D2EHPA diluted in hexane. In 1-decanol, this synergism was absent. Interactions of the second carrier with the extracted metal complex can occur for instance by replacement of the coordinated neutral extractant molecules and/or water molecules or by transformation of the coordination geometry.

Furthermore, the influence of the presence of acetate ions in the aqueous phase was studied. Besides the effect (Na, H) acetate can have on the extraction of metal ions, the participation of the aqueous phase ligands in the formation of the metal-organic complexes was investigated. The introduction of acetate ions in the aqueous phase showed the most profound effect on the extraction results of nickel(II), cobalt(II) and magnesium(II) with D2EHPA and LIX 860-I due to the presence of the (Na, H) acetate buffer. No evidence was found that supported an active role of acetate/acetic acid in the complex formation. In the case of iron(III, II), the higher extraction results in the presence of acetate could not be explained on the basis of the presence of the buffering agent. Furthermore, acetate ions only increased the extraction in 1-decanol (most profound effect with iron(III) – to a smaller extent for iron(II) and magnesium(II)). This indicates that interactions between the metal complex and acetic acid cannot be excluded in the presence of 1-decanol, especially in the case of iron(III).

In a further study on copper(II), cobalt(II), nickel(II) and iron(III), two different methods were applied to define the stoichiometry of the metal-organic complexes. The first method, Job's method, is based on the fact that the optical properties of complexes differ from that of the constituents. This spectrophotometric method was compared with a water-free procedure. By following up the release of hydrogen chloride during complexation, a correlation is obtained with the number of extractant molecules participating in the complexes.

Results of Job's method showed that complexes with an extractant:metal ratio of 1:1 were found for iron(III) extraction with D2EHPA and CYANEX 272 instead of a ratio of 3:1, which would be expected in order to maintain the electrical neutrality of the membrane phase. The absence of changes in chloride concentrations in the aqueous phases during extraction inferred the participation of hydroxyl ions in the extraction mechanism. Higher extractant participation (2:1 or 4:1) was noticed in the case of the iron(III) complexes with the thiosubstituted organosphinic reagents. The lower pH at which the experiments were performed and/or oxidation/reduction processes can declare the higher ligand participation.

To eliminate any hydrolysis, a further study was made under water-free circumstances. These experiments showed that 1:1 extractant:iron(III) complexes are easily formed. A further exchange towards higher extractant ratios was also observed, although the reaction proceeded remarkable slower. This indicated that higher extractant coordination is

also possible depending on the extractant type. In fact, the existence of $[FeCl_2L]$, $[FeClL_2]$ and to a smaller extent $[FeL_3]$ was assumed.

In the case of copper(II), mostly $[CuL_2]$ complexes have been distinguished with Job's method whereas in the case of cobalt(II) and nickel(II), 2:1 or 4:1 extractant:metal ratios were defined depending if either water or neutral extractant molecules were responsible for the solvatation process of the metal-organic complex. During the water-free experiments, $Cl^-:M^{n+}$ ratios of 2:1 were not achieved for copper(II), nickel(II) and cobalt(II). A major drawback of the anhydrous procedure is that the dissolution of the metal is depending upon the ease of extraction. Another parameter which may affect the extractant:metal ratio is the ease of release of hydrogen chloride during the experimental process. This can differ for the various extractants.

In general, it can be concluded that Job's method gives a more representative view on the stoichiometry of the metal-organic complexes during liquid-liquid extraction compared to the water-free procedure. This last method can however be used to declare any unusual complexation behaviour, as observed during the extraction of iron(III) with D2EHPA and CYANEX 272. Both methods confirmed that the formation of 1:1 neutral extractant:iron(III) complexes is possible.

Besides the two more fundamental research topics, a practical application of the Supported Liquid Membrane technology has been investigated, viz. the recovery of nickel(II) and its selectivity towards alkaline earth metal ions, viz. magnesium(II).

Liquid-liquid extraction experiments showed that commercial available extractants exhibit rather limited extraction efficiencies for nickel(II). However, if mixtures of organophosphorous acid extractants and hydroxyoximes were combined in the organic extractant solution, synergistic enhancements in the extraction of nickel(II) were noticed. In the presence of the organophosphoric acid D2EHPA in the extractant mixture, high distribution coefficients for nickel(II) were achieved, although this type of carrier shows only a limited selectivity for nickel(II) over alkaline earth metal ions. A better selectivity was achieved with an organophosphinic acid extractant, such as CYANEX 272 and CYANEX 302. However, lower distribution coefficients for nickel(II) were obtained compared to the presence of D2EHPA in the reagent mixture. If different types of hydroxyoximes are considered, the aldoxime (LIX 860-I) showed slightly higher extraction percentages compared to the ketoxime (LIX 84-I) when combined with an organophosphorous extraction reagent.

The results with SLM confirmed the conclusions of the liquid-liquid extraction experiments. Furthermore, it was shown that the nickel(II) flux can be improved by increasing the carrier concentration. However, the increase of the carrier concentration is limited (0.6 $mol.L^{-1}$) due to effects of steric hindrance and/or an increase of the viscosity of the liquid film. Furthermore, the results on real effluent streams have shown that nickel(II) can be recovered out of industrial effluents below the PARCOM value of 0.5 $mg.L^{-1}$ with a mixture of LIX 860-I and CYANEX 302. Also the stability of the liquid membrane was checked during 2600 hours. Fluxes can be achieved of 0.05 – 0.1 $g.m^{-2}.h^{-1}$ for the first 1500 hours. However, the nickel(II) flux showed a decreasing trend. The major reason for a Supported Liquid Membrane to become instable is the loss of the liquid membrane (extractant and/or solvent) out of the pores of the support.

Finally an introduction has been given into the potential abilities of Polymer Inclusion Membranes (PIM) and Immobilized Liquid Membranes (ILM) as alternative waste water treatment techniques. The major goals of Polymer Inclusion and Immobilized Liquid Membranes are to improve the long-term stability of the membrane and to maximize the membrane fluxes of the corresponding Liquid Membrane system.

The research on Polymer Inclusion Membranes was focussed on the development of a new PIM membrane with LIX 860-I as ligand for the extraction of copper(II). As polymer and plasticizer, polyvinylchloride and tri(2-n-butoxyethyl)phosphate (TBEP) were used, respectively. The results have shown that an increase of the carrier concentration can improve the copper(II) flux. However, very high carrier concentrations cannot be reached because otherwise the plasticizer and/or polymer concentration and/or thickness of the membrane is affected. At the same time, a minimal plasticizer concentration (20%) must be present, otherwise the membrane becomes too rigid and the metal flux is hindered. On the other hand, a high plasticizer concentration (30%) affected the stripping process in a negative way. Furthermore, thinner membranes are beneficial to the metal transport. Fluxes in the range of 0.1-0.2 $g.m^{-2}.h^{-1}$ were reached for copper(II) with PIM membranes while a flux of 3 $g.m^{-2}.h^{-1}$ was obtained with the corresponding SLM system.

The experimental work on Immobilized Liquid Membranes consisted of the chemical modification of an ethylenetetrafluoroethylene (ETFE) membrane grafted with vinylbenzylchloride (Solvay) and a polysulfone membrane, Desal E-500 (Desalination Systems). The modification route of the ETFE membrane grafted with vinylbenzylchloride involved the amination of the polymer membrane with liquid ammonia followed by the

anchoring of 5-bromo-2-hydroxybenzaldehyde onto the polymer backbone. For the amination process, a substitution degree of 60% of the available chloride functional groups was reached at 50°C and 100°C (30 and 60 bar, respectively). As far as the anchoring itself is considered, a final substitution degree of 20% was obtained compared to the initial available chloride functions. SLM-shaking experiments showed however a very restricted copper(II) transport. This was also the case with the corresponding non-modified ETFE membrane which was impregnated with LIX 860-I, suggesting that the thickness and/or porosity of the polymer membrane and/or a too low density of active groups restricted the copper(II) transport.

The modification route of the polysulfone membrane involved the direct lithiation of the membrane followed by its amination with tosyl azide and its subsequent reduction with sodium borohydride. Then, the anchoring of a chelating agent, 8-hydroxyquinoline, could be performed. The experimental work showed that the modification of a polymer membrane is much more difficult to achieve compared to the modification of its respective powder form due to the absence of a homogeneous reaction mixture (dissolution of all reagents) and the slow diffusion of reagents in the polymer membrane for modification. Furthermore, the choice of reaction solvent is rather limited in the case of Desal E-500 in order to maintain its membrane configuration. Only hexane could be applied for the modification route. However, no modification of the polymer membrane was observed. In the case of polysulfone UDEL 1700 - the corresponding pellet form - FT-IR as well as elemental analysis showed a substitution degree of 1.7 of the polymer unit for the aminated polysulfone. After the final anchoring of 8-hydroxyquinoline, batch extraction experiments were performed to determine the extent of copper(II) extraction. 1 g of aminated polysulfone was able to extract 0.25 mg copper(II). The modified polysulfone with 8-hydroxyquinoline showed no metal extraction.

This preliminary research on Polymer Inclusion and Immobilized Liquid Membranes gives already a first indication on the effectiveness of these technologies compared to Supported Liquid Membranes. The results indicated however that it seems very doubtful that fluxes in the same order of magnitude will be reached as for Supported Liquid Membranes. PIM-experiments have shown that the fluxes were at least one order of magnitude lower compared to SLM. Also with Immobilized Liquid Membranes, the extent of copper(II) extraction was very limited. In ILM, a different transport mechanism is involved compared to SLM, namely a “fixed-site jumping” mechanism instead of mobile carrier diffusion. This implies that a certain carrier concentration level must be reached in order to assure the

transport of the solutes across the membrane. Further research is necessary in order to increase the extent of modification.

Chapter 8

SAMENVATTING EN CONCLUSIES

Zware metalen zijn dikwijls aanwezig in tal van afvalstromen afkomstig van de metaalverwerkende nijverheid, textielsector, enz. Deze afvalstromen vormen een ernstige bedreiging voor het leefmilieu vanwege hun hoge giftigheid en talrijke verspreiding. Vanuit de overheid worden echter steeds strengere normen opgelegd inzake milieubeleid. Dit geeft tot gevolg dat bedrijven hun bestaande afvalwatersysteem dienen te optimaliseren. De klemtoon ligt hierbij voornamelijk op het implementeren van geïntegreerde processen in plaats van behandelingen die pas plaats vinden op het einde van het industriële proces. Niet enkel moet er gekeken worden naar de verwijdering van de metaalionen, maar ook naar een eventuele herbruikbaarheid in de industriële processen. Het hergebruik heeft als bijkomend voordeel dat natuurlijke bronnen behouden blijven. Vandaar dat er de laatste jaren zeer veel onderzoek wordt verricht naar nieuwe technologieën die deze doelstellingen kunnen bereiken. Eén van deze nieuwere technologieën is de Gedragen Vloeibare Membraantechnologie (Supported Liquid Membranes - SLM).

De Gedragen Vloeibare Membraantechnologie is een technologie die afgeleid werd van conventionele vloeistof-vloeistof extractiemethodes. Hierbij wordt gebruik gemaakt van een hydrofoob microporeus membraan – veelal polypropyleen - dat dienst doet als dragermateriaal voor het extractant of complexerend ligand. Aan de ene zijde van het membraan wordt het afvalwater (voeding) gestuurd, aan de andere zijde een zure oplossing, ook wel stripoplossing genoemd. Aan het interfasenvlak tussen de voeding en het membraan gebeurt de complexering tussen het metaalion en het extractant. Dit complex diffundeert doorheen het organisch membraan tot het metaalcomplex ontbonden wordt aan het interfasenvlak tussen het membraan en de stripoplossing. Op deze wijze worden de metaalionen getransporteerd vanuit de voeding naar een geconcentreerde stripoplossing. De protonen zorgen voor de drijvende kracht voor het transport van de metaalionen vanuit de voeding naar de stripoplossing, dit tegen hun eigen concentratiegradiënt in. De Gedragen Vloeibare Membraantechnologie biedt dus als belangrijk voordeel dat zeer verdunde afvalstromen efficiënt kunnen behandeld worden. Bovendien gebeurt de complexering en het

ontbinden van het complex simultaan, dit in tegenstelling tot de conventionele extractiemethodes en is een veel lagere hoeveelheid extractant vereist, wat de kostprijs aanzienlijk reduceert of het gebruik van duurdere extractanten toelaat.

Het talrijke onderzoek omtrent de SLM-technologie heeft reeds zeer goede resultaten aangetoond voor de verwijdering van koperionen uit afvalwater. Voor andere metaalionen, zoals bijvoorbeeld nikkel en kobalt, werden slechts lage metaalfluxen bereikt. De nood aan technieken voor metaalverwijdering in hydrometallurgische processen en in de behandeling van afvalwater heeft geleid tot tal van wetenschappelijke studies. De extractie-omstandigheden kunnen echter zeer uiteenlopend zijn en de voorgestelde extractiemechanismen zijn niet altijd éénduidig. Daarom wordt in dit huidige werk dieper ingegaan op de vorming van enkele metaalcomplexen die toepasbaar zijn in de Gedragen Vloeibare Membraantechnologie. Deze studies werden hoofdzakelijk toegespitst op de metaalionen koper(II), nikkel(II), kobalt(II), ijzer(III, II) en magnesium(II). Als extractanten werden hoofdzakelijk D2EHPA [di(2-ethylhexyl)fosforzuur], CYANEX 272 [di(2,4,4-trimethylpentyl)fosforigzuur], CYANEX 302 en CYANEX 301 (het respectievelijke monothio- en dithioderivaat van CYANEX 272) en LIX 860-I (5-dodecylsalicylaldoxime) bestudeerd.

In eerste instantie werd het complexeergedrag van deze individuele liganden ten opzichte van koper(II), nikkel(II), kobalt(II), ijzer(III, II) en magnesium(II) vergeleken met de aanwending van een mengsel van liganden. Zowel hexaan als 1-decanol werden gebruikt als solvent voor deze extractanten. Op deze manier kan de invloed van de polariteit van het solvent op de extractie van deze metaalionen en het gevormde complex onderzocht worden. FT-IR en UV-VIS absorptiespectra van de organische fasen werden aangewend voor de karakterisatie van de metaalcomplexen.

Enkele opmerkelijke verschillen werden vastgesteld wat betreft de extraheerbaarheid van enkele metaalionen wanneer hexaan of 1-decanol werd aangewend als solvent. Koper(II), ijzer(III), kobalt(II) en magnesium(II) worden bijvoorbeeld moeilijker geëxtraheerd met LIX 860-I in 1-decanol in vergelijking met hexaan. Interacties tussen het solvent en het extractant kunnen de extraheerbaarheid van de metaalionen negatief beïnvloeden. LIX 860-I kan interacties aangaan met een solvent met electron-donor eigenschappen, zoals ethanol of 1-decanol. Deze interacties beïnvloeden het aantal vrije extractantmoleculen en resulteren als dusdanig in een dalende extractie-efficiëntie. Het solvent kan ook een duidelijke invloed hebben op het type complex dat gevormd wordt. Dit kan geïllustreerd worden aan de hand

van de extractie van kobalt(II) met D2EHPA. In tegenstelling tot de eerder besproken solvent-extractant interacties treden nu interacties op tussen het solvent en het metaalcomplex. Een tetraedrisch kobalt(II)-D2EHPA complex wordt gevormd in hexaan, terwijl een octaedrisch complex gevormd wordt in 1-decanol.

Mengsels van twee of meerdere extractanten kunnen leiden tot synergistische effecten. Dit fenomeen werd vooral opgemerkt tijdens de extractie van nikkel(II) met een mengsel van LIX 860-I en D2EHPA. Het extractiepercentage bekomen met het mengsel van de extractanten was beduidend hoger dan de som van de bekomen extractiepercentages met de individuele liganden. Beide extractanten zijn betrokken in de complexvorming. Het ene extractant is verantwoordelijk voor de chelaatvorming, het andere ligand voor de solvatatie. Dit synergistisch effect werd enkel opgemerkt in hexaan en is dus ook afhankelijk van het type solvent.

Bovendien werd de invloed nagegaan van de toevoeging van additieven aan de waterige fase, zoals acetaationen. De aanwezigheid van acetaationen in de voeding vertoonde het meest uitgesproken effect op de extractieresultaten van nikkel(II), kobalt(II) en magnesium(II) met D2EHPA en LIX 860-I als extractant, dit omwille van de bufferwerking van (Na, H) acetaat. De buffer zorgt ervoor dat de pH voldoende hoog blijft (pH 4.0-5.0) voor de extractie van deze metaalionen met D2EHPA en LIX 860-I. Er werden echter geen aanwijzingen gevonden dat acetaat/azijnzuur ook een actieve rol speelt in de vorming van deze metaalcomplexen. Bij ijzer(III, II) daarentegen konden de hogere extractieresultaten in aanwezigheid van acetaat niet verklaard worden op basis van de bufferende werking van deze waterige additieven. Bovendien werden hogere extractieresultaten in aanwezigheid van acetaat enkel verkregen in 1-decanol (meest uitgesproken voor ijzer(III), in mindere mate voor ijzer(II) en zelfs magnesium(II)). Dit betekent dat interacties tussen voornamelijk het ijzer(III)complex en acetaat/azijnzuur niet uitgesloten kunnen worden in aanwezigheid van 1-decanol.

In het tweede deel van het onderzoek werden twee verschillende methodes toegepast om inzicht te verkrijgen in de stoichiometrie van de metaalcomplexen. Dit deel van het onderzoek werd uitgevoerd voor de metaalionen koper(II), nikkel(II), kobalt(II) en ijzer(III). Als eerste methode werd de methode van Job toegepast. Dit is een spectrofotometrische methode die gebruikt maakt van het feit dat de optische eigenschappen van de complexen verschillen van deze van de afzonderlijke componenten. De methode van Job werd vergeleken met een watervrije procedure waarbij de vrijstelling van zoutzuur tijdens de complexatie een maat is voor het aantal extractantmoleculen in het complex.

Met de methode van Job werd een extractant:metaal verhouding van 1:1 bekomen voor de extractie van ijzer(III) met D2EHPA en CYANEX 272, dit in tegenstelling tot een verhouding van 3:1 wat verwacht wordt op basis van de neutraliteit van het metaalcomplex. Er werd echter geen transport van de aanwezige waterige anionen, meerbepaald chloride ionen, vastgesteld. Dit impliceert dat hydroxylionen betrokken zijn in het extractiemechanisme. Een hogere extractant:metaal verhouding werd wel vastgesteld voor de extractie van ijzer(III) met de zwavelhoudende organische fosforigzuurderivaten. De lagere pH waarbij de extracties konden worden uitgevoerd en/of mogelijke oxidatie-reductieprocessen kunnen deze hogere ligand verhoudingen verklaren.

Om de hydrolyse van ijzer(III) ionen tegen te gaan, werden in een verdere studie dezelfde metaalcomplexen bestudeerd in watervrij milieu. Deze experimenten toonden aan dat ijzer(III) complexen met een extractant:metaal verhouding van 1:1 gemakkelijk gevormd worden. Een verdere uitwisseling tot hogere extractant:metaal verhoudingen werd ook vastgesteld, maar meestal was er slechts een trage evolutie merkbaar. Dit betekent dat hogere extractant:metaalverhoudingen wel mogelijk zijn afhankelijk van het type extractant. Eigenlijk gebeurt er een geleidelijke omzetting waarbij de aanwezigheid van $[FeCl_2L]$, $[FeClL_2]$ en in een kleinere mate $[FeL_3]$ wordt voorop gesteld.

Wat koper(II) betreft, werd hoofdzakelijk de vorming van $[CuL_2]$ complexen vastgesteld met de methode van Job. Kobalt(II) en nikkel(II) vormden metaalcomplexen met een extractant:metaalverhouding van 2:1 of 4:1 afhankelijk van het feit of watermoleculen of extractantmoleculen verantwoordelijk zijn voor de solvatatie van het metaalcomplex. Tijdens de watervrije procedures werd een extractant:metaal verhouding van 2:1 meestal niet bereikt voor koper(II), nikkel(II) en kobalt(II). Een belangrijk nadeel van de watervrije procedure is dat de oplosbaarheid van het metaalion afhankelijk is van de extraheerbaarheid van het metaalion en dus van de affiniteit van het extractant. Een andere belangrijke parameter die de $Cl^-:M^{n+}$ verhoudingen kan beïnvloeden is het gemak waarmee zoutzuur wordt vrijgesteld gedurende het experiment.

Algemeen kan gesteld worden dat de methode van Job een meer representatief beeld geeft van de stoichiometrie van de metaalcomplexen die gevormd werden tijdens de vloeistof-vloeistofextracties in vergelijking met de watervrije procedure. Deze watervrije procedure kan echter aangewend worden om een bepaald complexeergedrag te verklaren, zoals werd aangetoond voor de extractie van ijzer(III) met D2EHPA en CYANEX 272. Beide methodes bevestigden dat ijzer(III)-metaalcomplexen kunnen gevormd worden met een extractant:metaal verhouding 1:1.

In een derde luik werd een praktische toepassing van de Gedragen Vloeibare Membraantechnologie onderzocht, meerbepaald de extractie van nikkel(II) ionen en de overeenkomstige selectiviteit ten opzichte van aardalkalimetalen, zoals magnesium(II).

De vloeistof-vloeistofextracties toonden aan dat de commercieel beschikbare extractanten slechts een lage extraheerbaarheid vertonen voor nikkel(II). Daarentegen werden synergistische effecten opgemerkt bij het gebruik van een mengsel van extractanten, meerbepaald bij een combinatie van organische fosfor- of fosforigzuurderivaten en hydroxy-oximes. In aanwezigheid van D2EHPA, een organisch fosforzuur, werden hoge percentages nikkel(II) geëxtraheerd, maar werd slechts een beperkte selectiviteit bekomen ten opzichte van magnesium(II). Een betere selectiviteit werd bekomen met CYANEX 302 en CYANEX 272, twee organische fosforigzuurderivaten. Extractiepercentages voor nikkel(II) in de grootteorde zoals bij D2EHPA werden echter niet bereikt. Bij vergelijking van de hydroxy-oximes onderling werd een hoger extractierendement verkregen met een aldoxime (LIX 860-I) dan met het overeenkomstige ketoxime (LIX 84-I) in aanwezigheid van een organisch fosforzuurderivaat in de extractantoplossing.

Deze extractantmengsels werden ook uitgetest in SLM experimenten op laboschaal. Deze resultaten bevestigden de eerder bekomen resultaten met klassieke vloeistof-vloeistof extracties. Onderzoek naar de invloed van de concentratie van het extractant toonde aan dat de flux voor nikkel(II) stijgt in aanwezigheid van een hogere concentratie aan extractant. Een maximale flux werd bereikt bij een extractantconcentratie van 0.6 $mol.L^{-1}$. De daling van de flux bij hogere extractantconcentraties kan verklaard worden door sterische hindering en/of een eventuele verhoging van de viscositeit van het vloeibaar membraan. Finaal werden er SLM experimenten uitgevoerd op reële afvalstromen met een extractantmengsel bevattende LIX 860-I en CYANEX 302. De resultaten toonden aan dat nikkel(II) kan verwijderd worden uit afvalstromen met de Gedragen Vloeibare Membraantechnologie en dat de lozingsnormen opgelegd vanuit de overheid - 0.5 $mg.L^{-1}$ voor nikkel(II) - kunnen bereikt worden. Bovendien werd de stabiliteit van het vloeibaar membraan nagegaan gedurende 2600 uur. Nikkel(II) fluxen van 0.05 – 0.1 $g.m^{-2}.h^{-1}$ kunnen bereikt worden gedurende de eerste 1500 uur, hoewel er een geleidelijke daling werd opgemerkt. De belangrijkste reden voor de instabiliteit van de Gedragen Vloeibare Membraantechnologie is het verlies aan extractant en/of solvent vanuit de poriën van het dragermateriaal.

Tenslotte werd een voorbereidend onderzoek verricht naar de potentiële mogelijkheden van “Polymer Inclusion Membranes” (PIM) en “Immobilized Liquid Membranes” (ILM). Enerzijds kunnen deze aangepaste membraantechnologieën de stabiliteit

op lange termijn ten goede komen. Anderzijds wordt beoogd om de bestaande fluxen met het overeenkomstig gedragen vloeibaar membraan te maximaliseren.

PIM membranen worden gevormd door het oplossen van een mengsel van een polymeer, extractant en weekmaker in een aangepast solvent. Door het uitdampen van het solvent wordt een dun en flexibel membraan bekomen dat kan aangewend worden ter vervanging van het dragermateriaal dat doordrenkt wordt met de extractantoplossing in SLM. De belangrijkste doelstelling van deze verkennende studie was om een PIM membraan te ontwikkelen voor de extractie van koper(II) met LIX 860-I als extractant. Polyvinylchloride werd gebruikt als basispolymeer en tri(2-n-butoxyethyl)fosfaat als weekmaker. Een verhoging van de extractantconcentratie verhoogde de koper(II) flux. De stijging van de extractantconcentratie is echter beperkt met het oog op het behoud van de mechanische eigenschappen van het membraan. De concentratie aan weekmaker is eveneens belangrijk. Een minimale concentratie (20%) is essentieel om een flexibel membraan te bekomen. Bovendien werd vastgesteld dat een te lage concentratie aan weekmaker de metaalflux negatief beïnvloed. Anderzijds toonden de resultaten ook aan dat bij een te hoge concentratie aan weekmaker (30%) het stripproces wordt bemoeilijkt. Een reductie van de dikte van het membraan resulteerde in een hoger koper(II) transport. In het algemeen werden met de PIM membranen koperfluxen bekomen van 0.1 tot 0.2 $g.m^{-2}.h^{-1}$, terwijl met SLM een flux van 3 $g.m^{-2}.h^{-1}$ werd bereikt.

Het verkennend onderzoek naar de verankering van chelaterende liganden aan een polymeermembraan (ILM) heeft zich voornamelijk toegespitst op de modificatie van een ethyleentetrafluoroethyleen (ETFE) membraan dat voorzien werd van vinylbenzylchloride functionele groepen (Solvay) en op de modificatie van een polysulfonmembraan, Desal E-500 (Desalination Systems).

Voor de verankering van een chelaterend ligand aan het ETFE membraan werd het membraan eerst behandeld met vloeibare ammoniak voor de vorming van primaire aminogroepen, gevolgd door de verankering van 5-broom-2-hydroxybenzaldehyde. De aminering werd uitgevoerd bij 50°C (30 bar) en 100°C (60 bar). Met beide behandelingen werd een omzettingsgraad van 60% bereikt ten opzichte van het oorspronkelijke aantal aanwezige chloride functies. De tweede stap in het modificatieproces, meerbepaald de verankering zelf, leidde tot een finale omzettingsgraad van 20% (ten opzichte van het oorspronkelijke aantal chloride functies). De SLM schudproeven uitgevoerd met deze gemodificeerde membranen vertoonden echter een zeer beperkte koperflux. Het oorspronkelijke membraan doordrenkt met een oplossing van LIX 860-I vertoonde echter ook

een beperkte koperflux wat impliceert dat mogelijk de dikte en/of porositeit van het membraan aan de basis lag van dit beperkte metaaliontransport. Bovendien moet er een voldoende verankeringsgraad aanwezig zijn om een voldoende metaaltransport te verzekeren ("fixed-site jumping" mechanisme).

De modificatie van het polysulfonmembraan bestond uit een lithiering van het membraan, gevolgd door een aminering met tosyl azide en opeenvolgende reductie met natriumboorhydride. Na de aminering van het membraan vond de eigenlijke verankering van het ligand plaats. Hierbij werd gebruik gemaakt van 8-hydroxyquinoline. 2-hydroxybenzaldehyde kan evenwel ook verankerd worden via de modificatieroute die besproken werd voor het ETFE membraan. De resultaten toonden echter aan dat de modificatie van een polymeermembraan veel meer moeilijkheden vertoonde dan de functionalisatie van het overeenkomstige polymeerpoeder. Dit komt doordat de keuze aan solvent veel beperkter is voor het membraan met het oog op het behoud van de membraanconfiguratie. De modificatieprocedure voor het membraan Desal E-500 kon daarom enkel uitgevoerd worden in hexaan. Er werd echter geen succesvolle modificatie bekomen. Een vergelijkende studie werd uitgevoerd met het polysulfon UDEL 1700. De polymeereenheid vertoonde een omzettingsgraad van 1.7 na de amineringsstap. Voor het polysulfon UDEL 1700 kon de modificatieprocedure echter wel uitgevoerd worden in een homogeen milieu en kon tetrahydrofuraan als solvent worden aangewend. Na de verankering van het 8-hydroxyquinoline werden extractie-experimenten uitgevoerd met koper(II). 1g van het geamineerde polysulfon UDEL 1700 extraheerde 1.25 mg koper(II). Het polysulfon verankerd met 8-hydroxyquinoline vertoonde daarentegen geen koperextractie.

Op basis van deze verkennende studies omtrent PIM en ILM membranen kan gesteld worden dat het weinig waarschijnlijk lijkt dat deze twee technieken gelijkaardige fluxen kunnen bereiken als met Gedragen Vloeibare Membranen. De eerste resultaten met PIM membranen vertoonden 10 maal lagere koper(II) fluxen dan deze die werden bereikt met de overeenkomstige SLM procedure. De verkennende studies omtrent ILM membranen vertoonden zelfs een zeer beperkte koperextractie. Verder onderzoek met het oog op het verbeteren van de verankeringsgraad kan hierover uitsluitsel bieden.

LIST OF APPARATUS AND SPECIFICATIONS

ATOMIC ABSORPTION SPECTROSCOPY (AAS)

A Unicam 989 Atomic Absorption Spectrometer was used for the measurement of the metal concentrations in the aqueous phases.

pH-METER

pH measurements were performed with a Consort D714 pH meter with a calibrated glass combination electrode assembly.

INFRARED STUDIES (FT-IR)

Infrared spectral studies were carried out using a Perkin-Elmer 16 PC FT-IR.

UV-VIS STUDIES

Absorbance measurements were made with a Cary 100 Bio UV-Visible spectrophotometer from Varian with a 1-cm quartz cell.

TOTAL ORGANIC CARBON ANALYSIS (TOC)

TOC values were determined with a Schimadzu TOC-5000A Total Organic Carbon analyser.

SHAKING EXPERIMENTS

Shaking experiments were performed in a shaker at 305 rpm.

CAPILLARY ELECTROPHORESIS

Chloride concentrations in the aqueous phases were determined with a Waters Capillary Ion Analyser.

ELEMENTAL ANALYSIS

The nitrogen concentration of the polymer membranes was determined at ChevronTexaco Technology Ghent according to ASTM D5291 (CHNS).

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Annex A

Reagent data

Table A-1. Physical properties of D2EHPA (distributed by VWR International) [3_13]

Property	
D2EHPA content (w/w %)	97
Water content (w/w %)	0.08
Density at 20°C ($g.cm^{-3}$)	0.96
Molecular weight ($g.mol^{-1}$)	322.4
Viscosity at 20°C (mPa.s)	40
Flash point (°C)	approx. 180
Solubility (w/w %)	
D2EHPA in water at 20°C	< 0.1
Water in D2EHPA at 20°C	approx. 1.8

Table A-2. Physical properties of CYANEX reagents (CYTEC Canada Inc.) [3_12]

Property	CYANEX 272	CYANEX 302	CYANEX 301
CYANEX content (w/w %)	85	84	75-80
Density at 24°C ($g.cm^{-3}$)	0.92	0.93	0.95
Molecular weight ($g.mol^{-1}$)	290.4	306.5	322.6
pKa	6.37	5.63	2.61
Viscosity at 25°C (mPa.s)	142	195	78
Flash point (°C)	108	> 96	74
Solubility in water ($mg.L^{-1}$)	16	3	7

Table A-3. Physical properties of LIX Reagents (Cognis Inc.) [3_1]

Property	LIX 860-I	LIX 84-I
Oxime content (w/w %)	20.0	20.0
Density at 25°C ($g.cm^{-3}$)	0.92	0.91
Molecular weight ($g.mol^{-1}$)	305.5	265.4
Flash point (°C)	> 76	> 76

Table A-4. Physical properties of Versatic 10 (Shell Chemicals) [5_14]

Property	
Acid value (mg $KOH.g^{-1}$)	318-330
Water content (w/w %)	0.1 max.
Density at 20°C ($g.cm^{-3}$)	0.91
Molecular weight ($g.mol^{-1}$)	175
Viscosity at 20°C (mPa.s)	45
Flash point (°C)	129

Annex B

Influence of mixed extractant systems, acetate ions and type of solvent on the extraction data and corresponding equilibrium pH values of the metal ions copper(II), nickel(II), cobalt(II), magnesium(II) and iron(II,III)

Table B-1. Influence of acetate ions and type of solvent on the extraction of Cu(II) with different extractants or mixtures of extractants

	Without acetate		With 0.25 mol.L^{-1} acetate	
	%E	Equilibrium pH	%E	Equilibrium pH
D2EHPA				
Hexane	11	1.9	23	2.0
1-Decanol	13	1.9	29	2.2
LIX 860-I				
Hexane	99	1.0	99	0.98
1-Decanol	28	1.5	46	1.6
CYANEX 301				
Hexane	100	1.0	100	1.0
1-Decanol	100	1.1	100	1.1
D2EHPA/LIX 860-I				
Hexane	93	1.2	93	1.0
1-Decanol	28	1.5	41	1.6
CYANEX 301/LIX 860-I				
Hexane	100	1.0	100	1.00
1-Decanol	100	1.1	/	/
CYANEX 301/D2EHPA				
Hexane	100	1.2	100	1.1
1-Decanol	100	1.1	100	1.1

Table B-2. Influence of acetate ions and type of solvent on the extraction of Ni(II) with different extractants or mixtures of extractants

	Without acetate		With 0.25 mol.L^{-1} acetate	
	%E	Equilibrium pH	%E	Equilibrium pH
D2EHPA				
Hexane	4.6	2.3	83	4.4
1-Decanol	8.3	2.2	98	4.1
LIX 860-I				
Hexane	0.10	2.3	98	4.5
1-Decanol	0	2.3	45	4.9
CYANEX 301				
Hexane	81	1.2	100	4.4
1-Decanol	92	1.1	100	4.3
D2EHPA/LIX 860-I				
Hexane	34	1.7	100	4.3
1-Decanol	9.2	2.1	99	4.0
CYANEX 301/ LIX 860-I				
Hexane	74	1.1	100	4.2
1-Decanol	77	1.2	92	4.5
CYANEX 301/ D2EHPA				
Hexane	80	1.1	100	4.3
1-Decanol	100	4.3	100	4.2

Table B-3. Influence of increasing concentrations of acetate ions on the extraction of Ni(II) with different extractants or mixtures of extractants diluted in hexane

	Concentration of acetate in aqueous phase ($mol.L^{-1}$)				
	0	0.05	0.10	0.25	0.50
D2EHPA					
%E	4.6	32	56	83	82
Equilibrium pH	2.3	3.3	3.9	4.4	4.6
LIX 860-I					
%E	0.10	36	73	98	100
Equilibrium pH	2.3	2.9	3.3	4.5	4.7
CYANEX 301					
%E	81	83	90	100	99
Equilibrium pH	1.2	1.5	1.8	4.4	4.6
D2EHPA/LIX 860-I					
%E	34	51	84	100	100
Equilibrium pH	1.7	2.2	2.6	4.3	4.5
CYANEX 301/LIX 860-I					
%E	74	85	93	100	100
Equilibrium pH	1.1	1.5	2.1	4.2	4.7
CYANEX 301/D2EHPA					
%E	80	84	89	100	100
Equilibrium pH	1.1	1.5	2.0	4.3	4.4

Table B-4. Influence of acetate ions and type of solvent on the extraction of Co(II) with different extractants or mixtures of extractants

	Without acetate		With 0.25 mol.L^{-1} acetate	
	%E	Equilibrium pH	%E	Equilibrium pH
D2EHPA				
Hexane	6.0	2.3	90	4.4
1-Decanol	1.2	2.4	90	4.5
LIX 860-I				
Hexane	14	2.8	80	4.4
1-Decanol	1.3	4.2	3.9	5.1
CYANEX 301				
Hexane	58	1.2	99	4.2
1-Decanol	75	1.2	100	4.3
D2EHPA/LIX 860-I				
Hexane	11	1.9	100	4.2
1-Decanol	0	2.2	93	4.4
CYANEX 301/LIX 860-I				
Hexane	21	1.5	88	4.3
1-Decanol	78	1.2	86	4.4
CYANEX 301/D2EHPA				
Hexane	9.9	1.2	99	4.1
1-Decanol	97	1.1	100	4.1

Table B-5. Influence of the type of ligand added to the aqueous phase on the extraction of cobalt(II)

Buffer	D2EHPA	LIX 860-I	D2EHPA/ LIX 860-I
No addition			
%E	6.0	14	11
Equilibrium pH	2.3	2.8	1.9
***Formiat*e**			
%E	71	54	98
Equilibrium pH	3.7	3.8	3.7
Acetate			
%E	90	80	100
Equilibrium pH	4.4	4.4	4.2
Propionate			
%E	94	90	100
Equilibrium pH	4.3	4.4	4.0
Butyrate			
%E	84	90	100
Equilibrium pH	4.4	4.6	4.2
Lactate			
%E	53	42	50
Equilibrium pH	3.9	4.0	3.7

Table B-6. Influence of acetate ions and type of solvent on the extraction of Fe(III) with different extractants or mixtures of extractants

	Without acetate		With 0.25 mol.L^{-1} acetate	
	%E	Equilibrium pH	%E	Equilibrium pH
D2EHPA				
Hexane	99	0.87	99	0.88
1-Decanol	/	/	95	0.83
LIX 860-I				
Hexane	46	1.0	46	1.1
1-Decanol	0	1.7	47	1.5
CYANEX 301				
Hexane	71	0.90	61	0.91
1-Decanol	65	0.94	68	1.0
D2EHPA/LIX 860-I				
Hexane	95	0.87	95	0.82
1-Decanol	6.9	1.0	99	0.84
CYANEX 301/LIX 860-I				
Hexane	77	0.90	68	0.96
1-Decanol	73	0.98	81	0.92
CYANEX 301/D2EHPA				
Hexane	95	0.83	94	0.85
1-Decanol	82	0.95	96	0.89

Table B-7. Influence of acetate ions and type of solvent on the extraction of Fe(II) with different extractants or mixtures of extractants

	Without acetate		With 0.25 mol.L^{-1} acetate	
	%E	Equilibrium pH	%E	Equilibrium pH
D2EHPA				
Hexane	31	1.2	44	1.5
1-Decanol	21	1.4	6.7	1.7
LIX 860-I				
Hexane	2.0	1.2	8.5	1.7
1-Decanol	11	1.4	45	1.7
CYANEX 301				
Hexane	28	1.1	40	1.5
1-Decanol	53	1.1	39	1.4
D2EHPA/ LIX 860-I				
Hexane	42	1.1	43	1.5
1-Decanol	24	1.4	9.7	1.6
CYANEX 301/LIX 860-I				
Hexane	34	1.0	38	1.1
1-Decanol	26	1.4	77	1.4
CYANEX 301/ D2EHPA				
Hexane	59	1.1	59	1.5
1-Decanol	19	1.4	77	1.4

Table B-8. Influence of acetate ions and type of solvent on the extraction of Mg(II) with different extractants or mixtures of extractants

	Without acetate		With 0.25 mol.L^{-1} acetate	
	%E	Equilibrium pH	%E	Equilibrium pH
D2EHPA				
Hexane	30	2.2	86	4.2
1-Decanol	9.7	2.3	95	4.0
LIX 860-I				
Hexane	12	4.7	1.0	4.9
1-Decanol	2.9	5.3	0	5.1
CYANEX 301				
Hexane	13	2.5	3.5	4.8
1-Decanol	4.5	2.4	83	4.2
D2EHPA/ LIX 860-I				
Hexane	21	2.2	80	4.1
1-Decanol	8.1	2.3	/	/
CYANEX 301/ LIX 860-I				
Hexane	9.3	3.1	13	4.8
1-Decanol	14	2.5	76	4.3
CYANEX 301/D2EHPA				
Hexane	13	2.3	88	4.2
1-Decanol	39	1.9	100	3.6

Annex C

Extraction results of Job's method

Table C-1. Fe(III)-D2EHPA

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.186	22.3	0.046	22.3	1.7	100	4.9×10^2	38	1.6
0.20	0.303	46.1	0.415	45.7	1.6	99	1.1×10^2	11	1.1
0.25	0.371	61.9	2.43	59.4	1.6	96	25	3.0	0.5
0.30	0.369	69.6	5.76	63.8	1.5	92	11	1.6	0.20
0.33	0.407	74.9	10.0	64.8	1.5	87	6.5	1.0	**-0.002**
0.40	0.532	87.8	21.4	66.4	1.5	76	3.1	0.59	**-0.23**
0.50	0.571	113	42.7	70.5	1.5	62	1.7	0.48	**-0.32**
0.60	0.518	135	69.9	65.3	1.6	48	0.94	0.43	**-0.37**

Mean value log K = -0.23 ± 0.16

Table C-2. Cu(II)-D2EHPA

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.149	51.5	48.5	3.00	1.9	6.0	0.07	5.5×10^{-5}	**-4.3**
0.20	0.169	101	96.9	3.13	2.0	3.1	0.03	2.5×10^{-5}	**-4.6**
0.30	0.175	150	147	2.51	1.9	1.7	0.02	2.8×10^{-5}	**-4.6**
0.33	0.177	165	149	16.3	1.9	9.8	0.11	2.1×10^{-4}	**-3.7**
0.40	0.163	203	190	12.9	1.9	6.3	0.07	1.6×10^{-4}	**-3.8**
0.50	0.141	250	234	16.2	2.0	6.5	0.07	1.7×10^{-4}	**-3.8**
0.60	0.119	301	273	28.0	1.9	9.2	0.10	6.6×10^{-4}	**-3.2**
0.70	0.080	349	335	15.5	1.9	4.5	0.05	5.7×10^{-4}	**-3.2**
0.80	0.047	400	389	10.6	1.8	2.7	0.03	11×10^{-4}	**-3.0**

Mean value log K = -3.8 ± 0.59

Table C-3. Ni(II)-D2EHPA

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.282	51.8	4.64	47.1	3.9	91	11	8.0×10^{-7}	-6.1
0.20	0.408	107	32.9	73.9	3.8	69	2.3	1.4×10^{-6}	**-5.9**
0.30	0.419	160	77.8	82.4	3.6	52	1.1	1.2×10^{-6}	**-5.9**
0.40	0.395	207	131	75.1	3.5	36	0.57	2.3×10^{-6}	**-5.6**
0.50	0.354	256	199	56.9	3.5	22	0.29	1.4×10^{-6}	**-5.9**
0.60	0.301	286	242	43.9	3.5	15	0.18	1.3×10^{-6}	**-5.9**
0.70	0.233	323	305	18.2	3.6	5.6	0.06	1.2×10^{-7}	-6.4

Mean value log K = -5.8 ± 0.11

Table C-4. Co(II)-D2EHPA

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.885	5.04	2.06	2.96	4.7	59	1.4	5.2×10^{-7}	**-6.3**
0.20	1.68	10.8	3.70	7.09	4.6	66	1.9	1.6×10^{-6}	**-5.8**
0.30	2.01	16.3	8.15	8.15	4.6	50	1.0	2.0×10^{-6}	**-5.7**
0.40	2.08	22.3	14.1	8.17	4.6	37	0.58	2.2×10^{-6}	**-5.7**
0.50	1.88	27.0	20.0	7.06	4.7	26	0.35	1.7×10^{-6}	**-5.8**
0.60	1.48	31.3	26.2	5.14	4.6	16	0.20	1.5×10^{-6}	**-5.8**
0.70	1.16	36.7	32.9	3.78	4.6	10	0.12	8.7×10^{-7}	**-6.1**
0.80	0.712	41.4	39.6	1.82	4.6	4.4	0.05	8.7×10^{-7}	-6.1

Mean value log K = -5.9 ± 0.22

Table C-5. Fe(III)-CYANEX 272

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.105	4.98	0.48	4.50	1.7	90	9.3	3.6	**0.56**
0.20	0.383	10.0	1.00	9.02	1.6	90	9.0	4.6	**0.66**
0.30	0.611	15.0	2.18	12.8	1.6	86	5.9	4.2	**0.62**
0.40	0.763	20.1	4.01	16.1	1.5	80	4.0	4.6	**0.66**
0.45	0.804	22.6	5.49	17.1	1.6	76	3.1	4.7	**0.68**
0.70	0.530	35.3	23.9	11.4	1.8	32	0.48	2.1	**0.32**

Mean value log K = 0.57 ± 0.11

Table C-6. Cu(II)-CYANEX 272

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.20	/	106	100	5.62	2.8	5.3	0.06	8.4×10^{-7}	**-6.1**
0.25	0.157	133	127	5.71	2.8	4.3	0.04	7.6×10^{-7}	**-6.1**
0.30	0.171	158	152	5.89	2.9	3.7	0.04	6.6×10^{-7}	**-6.2**
0.33	0.178	173	167	6.78	2.9	3.9	0.04	6.7×10^{-7}	**-6.2**
0.40	0.178	204	201	3.30	2.9	1.6	0.02	4.3×10^{-7}	**-6.4**
0.50	0.163	258	257	0.535	2.9	0.2	0.002	5.7×10^{-8}	**-7.3**
0.70	0.090	342	348	0	2.9	/	/	/	/

Mean value log K = -6.4 ± 0.44

Table C-7. Co(II)-CYANEX 272

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.345	5.12	3.92	1.20	4.7	24	0.31	7.1×10^{-8}	**-7.2**
0.20	0.526	8.96	7.32	1.65	4.7	18	0.22	7.9×10^{-8}	**-7.1**
0.25	0.569	12.5	10.8	1.78	4.7	14	0.17	6.6×10^{-8}	**-7.2**
0.30	0.588	15.8	13.8	1.90	4.7	12	0.14	6.6×10^{-8}	**-7.2**
0.33	0.588	16.5	14.6	1.95	4.7	12	0.13	6.3×10^{-8}	**-7.2**
0.40	0.563	21.5	19.7	1.80	4.7	8.2	0.09	4.6×10^{-8}	-7.3
0.70	0.272	35.2	34.1	1.10	4.7	3.1	0.03	6.8×10^{-8}	-7.2

Mean value log K = -7.2 ± 0.04

Table C-8. Fe(III)-CYANEX 302

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.553	4.87	4.70	0.166	0.78	3.4	0.04	0.18	**-0.75**
0.20	0.849	9.71	9.17	0.541	0.85	5.6	0.06	0.39	**-0.41**
0.25	0.938	12.4	11.6	0.788	0.90	6.3	0.07	0.53	**-0.28**
0.30	0.972	14.7	13.6	1.10	1.0	7.5	0.08	0.76	**-0.12**
0.33	0.960	16.2	15.0	1.15	0.81	7.1	0.08	0.79	**-0.10**
0.40	0.958	19.4	18.6	0.738	0.93	3.8	0.04	0.49	**-0.31**
0.70	0.267	34.2	34.2	0.025	0.80	0.07	0	/	/

Mean value log K = -0.32 ± 0.24

Table C-9. Cu(II)-CYANEX 302

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	/	5.14	0	5.14	2.0	100	1.0×10^5	/	/
0.20	/	10.4	0	10.4	2.0	100	1.0×10^5	/	/
0.25	/	13.3	0	13.3	2.0	100	1.0×10^5	/	/
0.30	/	15.8	2.81	13.0	2.0	82	4.6	1.7×0^{-5}	**-4.8**
0.33	/	17.1	4.91	12.2	2.0	71	2.5	8.9×10^{-6}	**-5.1**
0.40	/	21.4	10.1	11.2	2.0	53	1.1	5.9×10^{-6}	**-5.2**
0.50	/	25.4	16.6	8.84	2.0	35	0.53	3.0×10^{-6}	**-5.5**
0.60	/	30.6	24.2	6.46	2.0	21	0.27	1.6×10^{-6}	**-5.8**

Mean value log K = -5.3 ± 0.40

Table C-10. Ni(II)–CYANEX 302

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.775	50.6	44.5	6.03	4.0	12	0.14	4.1×10^{-8}	**-7.4**
0.20	0.936	102	92.9	8.80	4.0	8.7	0.09	5.4×10^{-8}	**-7.3**
0.25	0.954	125	111	13.1	4.0	11	0.12	1.1×10^{-7}	**-7.0**
0.30	0.895	150	139	11.4	4.0	7.6	0.08	9.6×10^{-8}	**-7.0**
0.33	0.744	165	155	9.86	3.9	6.0	0.06	8.3×10^{-8}	**-7.1**
0.40	0.497	201	193	7.90	3.9	3.9	0.04	7.9×10^{-8}	**-7.1**

Mean value log K = -7.0 ± 0.35

Table C-11. Co(II)-CYANEX 302

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.351	5.30	0.893	4.41	4.7	83	4.9	2.6×10^{-3}	**-2.6**
0.20	0.429	10.5	4.77	5.72	4.7	55	1.2	4.2×10^{-3}	**-2.4**
0.25	0.414	13.7	8.21	5.50	4.7	40	0.67	3.5×10^{-3}	**-2.5**
0.30	0.386	16.1	10.9	5.21	4.7	32	0.48	3.6×10^{-3}	**-2.5**
0.33	0.364	17.5	12.5	5.01	4.7	29	0.40	3.7×10^{-3}	**-2.4**
0.40	0.327	22.2	17.2	4.96	4.7	22	0.29	8.2×10^{-3}	**-2.1**
0.60	0.211	31.9	29.2	2.69	4.7	8.5	0.09	3.9×10^{-3}	-2.4

Mean value log K = -2.4 ± 0.17

Table C-12. Fe(III)-CYANEX 301

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.987	5.19	0.543	4.64	0.86	90	8.6	1.7×10^{3}	3.2
0.20	1.22	10.2	3.22	6.98	0.93	68	2.2	10×10^{3}	**4.0**
0.25	1.15	12.9	6.15	6.75	0.88	52	1.1	9.0×10^{3}	**4.0**
0.33	0.996	16.9	10.5	6.47	0.96	38	0.62	18×10^{3}	**4.3**
0.40	0.518	19.5	13.9	5.64	0.96	29	0.41	13×10^{3}	**4.1**
0.50	0.254	24.1	19.1	4.96	0.99	21	0.26	36×10^{3}	**4.6**
0.70	0.131	33.4	30.6	2.73	0.85	8.2	0.09	32×10^{3}	4.5

Mean value log K = 4.0 ± 0.44

Table C-13a. Cu(II)-CYANEX 301 (2:1 extractant:metal ratio)

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	1.08	4.99	0	4.99	2.0	100	1.0×10^5	/	/
0.20	1.38	13.1	0	13.1	2.0	100	1.0×10^5	/	/
0.25	0.972	15.6	0	15.6	2.0	100	1.0×10^5	/	/
0.30	0.736	17.0	0.02	17.0	2.0	100	7.3×10^2	/	/
0.40	0.560	21.1	4.60	16.5	2.0	78	3.6	4.3×10^2	2.6
0.50	0.482	26.6	12.0	14.5	2.0	55	1.2	12	**1.1**
0.60	0.368	31.7	20.4	11.3	2.0	36	0.55	11	**1.0**
0.70	0.296	36.2	27.8	8.40	2.0	23	0.30	12	**1.1**
0.80	0.214	41.4	35.0	6.43	2.0	16	0.18	3.2	**0.51**

Mean value log K = 0.92 ± 0.28

Table C-13b. Cu(II)-CYANEX 301 (4:1 extractant:metal ratio)

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	1.08	4.99	0	4.99	2.0	100	1.0×10^5	/	/
0.20	1.38	13.1	0	13.1	2.0	100	1.0×10^5	/	/
0.25	0.972	15.6	0	15.6	2.0	100	1.0×10^5	/	/
0.30	0.736	17.0	0.02	17.0	2.0	100	7.3×10^2	6.5×10^4	4.8
0.40	0.560	21.1	4.60	16.5	2.0	78	3.6	2.7×10^2	**2.4**
0.50	0.482	26.6	12.0	14.5	2.0	55	1.2	91×10^2	**2.0**
0.60	0.368	31.7	20.4	11.3	2.0	36	0.55	1.3×10^2	**2.1**
0.70	0.296	36.2	27.8	8.40	2.0	23	0.30	2.6×10^2	**2.4**
0.80	0.214	41.4	35.0	6.43	2.0	16	0.18	3.7×10^2	**2.6**

Mean value log K = 2.3 ± 0.25

Table C-14. Ni(II)-CYANEX 301

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start $mmol.L^{-1}$	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ $mmol.L^{-1}$	Equilibrium pH	%E	k	K	Log K
0.10	0.505	5.40	0	5.40	4.6	100	1.0×10^5	/	/
0.20	0.989	10.3	0.986	9.27	4.6	90	9.4	38	1.6
0.25	0.969	14.2	4.44	9.78	4.7	69	2.2	1.0×10^2	**2.0**
0.30	0.946	16.5	7.50	9.02	4.7	55	1.2	2.5×10^2	**2.4**
0.33	0.877	18.6	9.79	8.81	4.7	47	0.90	29	**1.5**
0.40	0.796	21.4	14.3	7.08	4.7	33	0.50	19	**1.3**
0.60	0.559	33.2	27.7	5.47	4.7	17	0.20	4.7	**0.67**

Mean value log K = 1.6 ± 0.67

Table C-15. Co(II)-CYANEX 301

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start $mmol.L^{-1}$	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ $mmol.L^{-1}$	Equilibrium pH	%E	k	K	Log K
0.10	0.280	4.29	0	4.29	4.7	100	1.0×10^5	/	/
0.20	0.503	9.43	0.02	9.41	4.7	100	4.3×10^2	4.0×10^{-4}	-3.4
0.30	0.567	13.6	3.17	10.5	4.7	77	3.3	8.4×10^{-6}	**-5.1**
0.40	0.499	20.0	10.5	9.47	4.7	47	0.90	2.9×10^{-6}	**-5.5**
0.50	0.423	25.7	17.5	8.16	4.8	32	0.47	2.0×10^{-6}	**-5.7**
0.60	0.341	30.7	24.4	6.30	4.7	21	0.26	1.6×10^{-6}	**-5.8**
0.70	0.255	35.4	31.0	4.36	4.8	12	0.14	1.1×10^{-6}	**-6.0**
0.80	0.173	39.2	37.4	1.83	4.8	4.7	0.05	3.7×10^{-7}	-6.4

Mean value log K = -5.6 ± 0.33

Table C-16. Fe(III)-LIX 860-I

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.969	4.11	0.853	3.26	0.88	79	3.8	88	**1.9**
0.20	1.11	8.65	4.64	4.01	0.85	46	0.86	39	**1.6**
0.25	1.13	10.9	6.70	4.24	0.88	39	0.63	42	**1.6**
0.30	1.08	12.6	9.37	3.22	0.93	26	0.34	21	**1.3**
0.33	0.977	14.4	12.5	1.89	0.91	13	0.15	7.0	**0.85**
0.40	0.881	16.8	15.4	1.39	0.87	8.3	0.09	5.2	0.72
0.50	0.686	22.1	20.2	1.82	0.89	8.3	0.09	12	1.1
0.60	0.458	24.8	28.0	0	0.92	/	/	/	/

Mean value log K = 1.5 ± 0.41

Table C-17. Cu(II)-LIX 860-I

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.544	5.45	0.01	5.44	2.1	100	5.5×10^2	37	1.6
0.20	1.15	10.3	0.07	10.2	2.0	99	1.5×10^2	98	2.0
0.30	1.48	15.3	1.65	13.6	2.0	89	8.2	15	**1.2**
0.40	1.37	20.9	8.43	12.5	2.0	60	1.5	5.1	**0.71**
0.50	1.15	26.7	15.4	11.3	2.0	42	0.73	14	**1.2**
0.60	0.917	32.1	23.1	8.98	2.0	28	0.39	10	**1.0**
0.70	0.772	36.0	29.8	6.24	2.0	17	0.21	3.4	**0.53**
0.80	0.459	42.1	37.1	5.04	2.0	12	0.14	1.4×10^3	**3.2**

Mean value log K = 1.2 ± 0.88

Table C-18. Ni(II)-LIX 860-I

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.645	5.28	0.061	5.22	4.6	100	85	5.4×10^{-5}	-4.3
0.20	1.29	10.4	0.291	10.1	4.5	97	35	8.4×10^{-5}	-4.1
0.30	1.63	15.5	2.44	13.1	4.6	84	5.4	4.6×10^{-5}	**-4.3**
0.40	1.52	20.6	8.72	11.9	4.6	58	1.4	2.1×10^{-5}	**-4.7**
0.50	1.28	25.8	15.0	10.8	4.6	42	0.72	3.6×10^{-5}	**-4.4**
0.60	1.07	29.3	22.0	7.33	4.6	25	0.33	7.3×10^{-6}	**-5.1**
0.70	0.805	35.4	29.3	6.05	4.6	17	0.21	1.9×10^{-5}	**-4.7**
0.80	0.533	39.7	35.2	4.55	4.6	12	0.13	1.3×10^{-4}	**-3.9**

Mean value log K = -4.5 ± 0.42

Table C-19. Co(II)-LIX 860-I

$c_M^{n+}/(c_M^{n+}+c_{HL})$	A	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L	$[M^{n+}]_o$ mmol.L^{-1}	Equilibrium pH	%E	k	K	Log K
0.10	0.702	5.01	1.88	3.13	4.6	63	1.7	5.5×10^{-10}	**-9.3**
0.20	0.821	10.0	6.46	3.58	4.6	36	0.55	2.9×10^{-10}	**-9.6**
0.25	0.828	12.4	8.84	3.60	4.6	29	0.40	2.8×10^{-10}	**-9.6**
0.30	0.838	15.0	11.6	3.40	4.7	23	0.29	2.2×10^{-10}	**-9.7**
0.33	0.802	16.5	13.2	3.33	4.6	20	0.25	2.5×10^{-10}	**-9.6**
0.40	0.656	20.1	17.7	2.35	4.6	12	0.13	1.6×10^{-10}	**-9.8**
0.50	0.621	25.2	23.9	1.35	4.7	5.4	0.06	4.9×10^{-11}	-10
0.70	0.291	35.0	34.1	0.961	4.8	2.7	0.03	8.4×10^{-11}	-10

Mean value log K = -9.6 ± 0.16

Annex D

Release of chloride ions as a function of time of water-free experiments

Table D-1. Fe(III)-D2EHPA

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.537	0.429
	2	0.871	0.697
	3	1.05	0.841
	4	1.17	0.932
	7	1.26	1.01
	23	1.28	1.02
2:1	24	1.34	1.07
	25	1.39	1.12
	26	1.44	1.15
	27	1.50	1.20
	30	1.60	1.28
	46	1.78	1.43
3:1	47	1.84	1.48
	48	1.86	1.49
	49	1.87	1.50
	50	1.89	1.51
	53	1.92	1.54
	69	2.00	1.60
Direct procedure			
3:1	1	0.337	0.269
	2	0.602	0.482
	3	0.806	0.645
	4	0.939	0.751
	7	1.21	0.969
	23	1.95	1.56

Table D-2. Cu(II)-D2EHPA

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.036	0.029
	2	0.038	0.031
	3	0.038	0.031
	4	0.038	0.031
	7	0.039	0.031
	23	0.044	0.035
2:1	24	0.044	0.035
	25	0.044	0.035
	26	0.044	0.035
	27	0.044	0.035
	30	0.044	0.035
	46	0.044	0.035
3:1	47	0.045	0.036
	48	0.045	0.036
	49	0.045	0.036
	50	0.045	0.036
	53	0.049	0.039
	69	0.056	0.045
4:1	70	0.058	0.047
	71	0.061	0.049
	72	0.061	0.049
	73	0.061	0.049
	76	0.064	0.051
	92	0.068	0.054
Direct procedure			
4:1	1	0.095	0.076
	2	0.106	0.085
	3	0.113	0.090
	4	0.120	0.096
	7	0.128	0.102
	23	0.137	0.101

Table D-3. Ni(II)-D2EHPA

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0	0
	2	0.001	0.001
	3	0.003	0.002
	4	0.003	0.002
	7	0.004	0.003
	23	0.006	0.005

Table D-4. Co(II)-D2EHPA

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0.067	0.054
	2	0.075	0.056
	3	0.082	0.066
	4	0.082	0.066
	7	0.084	0.067
	23	0.099	0.079

Table D-5. Fe(III)-CYANEX 272

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.278	0.224
	1.8	0.613	0.490
	2.6	0.774	0.619
	4.1	0.888	0.711
	7.1	1.05	0.840
	23.5	1.13	0.900
2:1	24.5	1.78	0.942
	25.5	1.18	0.946
	26.5	1.19	0.948
	27.5	1.19	0.950
	30.5	1.19	0.954
	46.5	1.20	0.958
3:1	47.5	1.20	0.960
	48.5	1.20	0.961
	49.5	1.20	0.962
	50.5	1.20	0.963
	53.5	1.21	0.965
	69.5	1.21	0.967
Direct procedure			
3:1	1	0.041	0.033
	2	0.104	0.083
	3	0.153	0.122
	4	0.194	0.155
	7	0.310	0.248
	23	0.375	0.300

Table D-6. Cu(II)-CYANEX 272

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.021	0.017
	2	0.032	0.026
	3	0.041	0.033
	4	0.051	0.041
	7	0.060	0.048
	23	0.047	0.056
Direct procedure			
4:1	1	0.008	0.006
	2	0.012	0.010
	3	0.015	0.012
	4	0.019	0.015
	7	0.025	0.020
	23	0.036	0.029

Table D-7. Fe(III)-CYANEX 302

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.428	0.343
	2	0.662	0.530
	3	0.763	0.611
	4	0.834	0.667
	7	1.01	0.806
	23.3	1.07	0.859
2:1	24.3	1.09	0.869
	25.3	1.09	0.869
	26.3	1.09	0.869
	27.3	1.09	0.875
	30.3	1.11	0.888
	46.3	1.11	0.888
3:1	47.3	1.11	0.890
	48.3	1.11	0.890
	49.3	1.11	0.890
	50.3	1.11	0.890
	53.3	1.12	0.897
	69.3	1.13	0.900
Direct procedure			
3:1	1	0.142	0.114
	2	0.334	0.267
	3	0.438	0.351
	4	0.573	0.458
	7	0.726	0.581
	23.2	0.776	0.621

Table D-8. Cu(II)-CYANEX 302

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.388	0.310
	2	0.576	0.460
	3	0.615	0.492
	4	0.651	0.521
	7	0.920	0.736
	23	1.07	0.852
2:1	24	1.14	0.913
	25	1.17	0.932
	26	1.17	0.937
	27	1.18	0.941
	30	1.25	0.997
	46	1.26	1.01
3:1	47	1.27	1.02
	48	1.27	1.02
	49	1.27	1.02
	50	1.28	1.03
	53	1.29	1.04
	69	1.30	1.04
4:1	70	1.31	1.04
	71	1.31	1.05
	72	1.31	1.05
	73	1.31	1.05
	76	1.31	1.05
	92	1.31	1.05
Direct procedure			
4:1	1	0.268	0.214
	2	0.402	0.322
	3	0.444	0.355
	4	0.476	0.380
	7	0.654	0.523
	23	0.668	0.534

Table D-9. Ni(II)-CYANEX 302

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0.001	0.001
	2	0.002	0.002
	7	0.016	0.012
	23	0.017	0.014

Table D-10. Co(II)-CYANEX 302

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0.004	0.003
	2	0.005	0.004
	3	0.008	0.006
	4	0.008	0.006
	7	0.012	0.009
	23	0.014	0.011

Table D-11. Fe(III)-CYANEX 301

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.593	0.475
	2	0.712	0.570
	3	0.731	0.585
	4	0.780	0.624
	7	0.862	0.690
	23	0.878	0.703
2:1	24	1.10	0.878
	25	1.19	0.955
	26	1.23	0.983
	27	1.26	1.00
	30	1.31	1.05
	46	1.34	1.08
3:1	47	1.39	1.11
	48	1.42	1.13
	49	1.44	1.16
	50	1.47	1.18
	53	1.54	1.23
	69	1.56	1.25
Direct procedure			
3:1	1	0.861	0.689
	2	1.12	0.899
	3	1.22	0.978
	4	1.33	1.07
	7	1.58	1.27
	23	1.72	1.38

Table D-12. Cu(II)-CYANEX 301

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.591	0.473
	2	0.705	0.564
	3	0.752	0.602
	4	0.781	0.625
	7	0.893	0.714
	23	1.06	0.849
2:1	24	1.43	1.14
	25	1.48	1.19
	26	1.51	1.21
	27	1.53	1.22
	30	1.63	1.31
	46	1.78	1.42
3:1	47	1.95	1.56
	48	1.99	1.59
	49	2.01	1.61
	50	2.02	1.62
	53	2.05	1.64
	69	2.08	1.67
4:1	70	2.08	1.67
	71	2.09	1.67
	72	2.09	1.67
	73	2.09	1.67
	76	2.09	1.67
	92	2.10	1.68
Direct procedure			
4:1	1	1.30	1.04
	2	1.49	1.19
	3	1.56	1.25
	4	1.62	1.30
	7	1.76	1.41
	23	1.99	1.60

Table D-13. Ni(II)-CYANEX 301

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0.035	0.028
	2	0.039	0.032
	3	0.042	0.033
	4	0.042	0.033
	7	0.044	0.035
	23	0.079	0.064

Table D-14. Co(II)-CYANEX 301

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0.008	0.006
	2	0.014	0.011
	3	0.016	0.013
	4	0.017	0.013
	7	0.107	0.085
	23	1.04	0.830

Table D-15. Fe(III)-LIX 860-I

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.048	0.039
	2	0.075	0.060
	3	0.092	0.073
	4	0.108	0.086
	7	0.158	0.126
	23	0.303	0.242
2:1	24	0.327	0.262
	25	0.339	0.271
	26	0.348	0.279
	27	0.357	0.285
	30	0.391	0.313
	46	0.541	0.433
3:1	47	0.563	0.450
	48	0.571	0.457
	49	0.579	0.463
	50	0.587	0.469
	53	0.611	0.489
	69	0.718	0.575
Direct procedure			
3:1	1	0.096	0.077
	2	0.118	0.094
	3	0.137	0.109
	4	0.160	0.128
	7	0.212	0.170
	23.4	0.308	0.246

Table D-16. Cu(II)-LIX 860-I

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Stepwise procedure			
1:1	1	0.057	0.045
	2	0.084	0.067
	3	0.101	0.081
	4	0.118	0.094
	7	0.267	0.213
	23	0.283	0.226
2:1	24	0.431	0.345
	25	0.454	0.363
	26	0.469	0.375
	27	0.523	0.418
	30	0.609	0.487
	46	0.685	0.548
3:1	47	0.699	0.559
	48	0.721	0.577
	49	0.780	0.600
	50	0.778	0.622
	53	0.913	0.730
	69	0.959	0.767
4:1	70	1.02	0.815
	71	1.09	0.875
	72	1.13	0.901
	73	1.15	0.921
	76	1.18	0.941
	92	1.37	1.09
Direct procedure			
4:1	1	0.229	0.183
	2	0.338	0.271
	3	0.391	0.313
	4	0.501	0.401
	7	0.674	0.539
	23	0.961	0.769

Table D-17. Ni(II)-LIX 860-I

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0.007	0.005
	2	0.010	0.008
	3	0.012	0.010
	4	0.014	0.012
	7	0.017	0.014
	23	0.034	0.027

Table D-18. Co(II)-LIX 860-I

Extractant:metal concentration ratio	Time (h)	Cl^- (mmol) Receiving solution (cumulative)	$Cl^-:M^{n+}$ M^{n+} = 1.25 mmol (cumulative)
Direct procedure			
4:1	1	0	0
	2	0	0
	3	0.001	0.001
	4	0.001	0.001
	7	0.002	0.002
	23	0.004	0.003

Annex E

Data of liquid-liquid extractions

Table E-1. Extraction efficiency of commercial hydroxyoxime and organophosphorous liquid ion exchangers

pH 5.0

Extractant	$[Ni^{2+}]_a$ At the start $mmol.L^{-1}$	$[Ni^{2+}]_a$ At the end $mmol.L^{-1}$	$[Ni^{2+}]_o$ $mmol.L^{-1}$	%E	k
LIX 84-I	8.54	8.55	0	0	0
LIX 860-I	8.54	8.44	0.094	1.1	0.01
D2EHPA	8.54	8.41	0.128	1.5	0.02
CYANEX 272	8.54	8.08	0.452	5.3	0.06
CYANEX 302	8.54	8.03	0.504	5.9	0.06
CYANEX 301	8.54	0	8.54	100	/

pH 7.0

Extractant	$[Ni^{2+}]_a$ At the start $mmol.L^{-1}$	$[Ni^{2+}]_a$ At the end $mmol.L^{-1}$	$[Ni^{2+}]_o$ $mmol.L^{-1}$	%E	k
LIX 84-I	8.53	5.53	3.00	35	0.54
LIX 860-I	8.53	7.38	1.14	13	0.16
D2EHPA	8.53	8.34	0.188	2.2	0.02
CYANEX 272	8.53	8.53	0	0	0
CYANEX 302	8.53	7.85	0.674	7.9	0.09
CYANEX 301	8.53	0.009	8.52	100	1.0×10^3

Table E-2. Influence of a mixture of D2EHPA and LIX 84-I on the extraction efficiency of nickel(II)

Extractant	Metal ion	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L^{-1}	$[M^{n+}]_o$ mmol.L^{-1}	%E	k
0.04 mol.L^{-1} LIX 84-I	Ni	8.57	8.31	0.268	3.1	0.03
	Mg	4.28	3.79	0.494	12	0.13
0.04 mol.L^{-1} D2EHPA	Ni	8.57	7.40	1.17	14	0.16
	Mg	4.28	1.34	2.94	69	2.2
0.04 mol.L^{-1} LIX 84-I + 0.04 mol.L^{-1} D2EHPA	Ni	8.57	0.870	7.70	90	8.9
	Mg	4.28	2.08	2.20	51	1.1

Table E-3. Influence of the type of organophosphorous acid in combination with LIX 84-I and comparison with the extraction efficiency of a carboxylic acid

Extractant: 0.04 mol.L^{-1} LIX 84-I +	Metal ion	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L^{-1}	$[M^{n+}]_o$ mmol.L^{-1}	%E	k
0.04 mol.L^{-1} D2EHPA	Ni	8.59	0.870	7.72	90	8.9
	Mg	4.26	2.08	2.18	51	1.0
0.04 mol.L^{-1} CYANEX 272	Ni	8.59	5.54	3.05	36	0.55
	Mg	4.26	4.05	0.206	4.8	0.05
0.04 mol.L^{-1} CYANEX 302	Ni	8.59	4.31	4.28	50	0.99
	Mg	4.26	3.91	0.350	8.2	0.09
0.04 mol.L^{-1} Versatic 10	Ni	8.59	8.22	0.370	4.3	0.04
	Mg	4.26	4.01	0.247	5.8	0.06

Table E-4. Influence of the type of oxime in combination with CYANEX 302

Extractant: 0.04 mol.L^{-1} CYANEX 302 +	Metal ion	$[M^{n+}]_a$ At the start mmol.L^{-1}	$[M^{n+}]_a$ At the end mmol.L^{-1}	$[M^{n+}]_o$ mmol.L^{-1}	%E	k
0.04 mol.L^{-1} LIX 84-I	Ni	8.59	4.31	4.28	50	0.99
	Mg	4.26	3.91	0.350	8.2	0.09
0.04 mol.L^{-1} LIX 860-I	Ni	8.57	3.45	5.13	60	1.5
	Mg	4.16	3.58	0.576	14	0.16

Annex F

Data of SLM experiments

Table F-1. Influence of the type of organophosphorous acid and hydroxyoxime when combined as extractant mixture in a flat membrane

Time (h)	Ni(II) concentration Feed ($mg.L^{-1}$)	Ni(II) concentration Strip ($mg.L^{-1}$)	Mg(II) concentration Strip ($mg.L^{-1}$)	Flux Ni(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Ni(II) Strip ($g.m^{-2}.h^{-1}$)	Flux Mg(II) Strip ($g.m^{-2}.h^{-1}$)
0.4 mol.L^{-1} LIX 84-I + 0.4 mol.L^{-1} D2EHPA						
0	501	0	0			
2.0	277	205	5.00	3.6	3.3	0.081
4.8	47.0	429	22.7	2.7	2.6	0.21
5.8	14.4	466	34.1	1.1	1.2	0.37
20.8	0	483	81.0	0.03	0.04	0.10
0.4 mol.L^{-1} LIX 84-I + 0.4 mol.L^{-1} CYANEX 272						
0	508	0	0			
2.3	332	162	1.25	2.4	2.2	0.017
3.0	291	202	1.55	2.0	1.9	0.014
4.0	226	259	2.09	2.1	1.8	0.017
5.0	181	298	2.58	1.5	1.3	0.016
5.8	157	326	2.91	1.1	1.2	0.014
20.9	0.95	471	32.6	0.33	0.31	0.063
0.4 mol.L^{-1} LIX 84-I + 0.4 mol.L^{-1} CYANEX 302						
0	502	0	0			
2.1	365	129	0	2.1	2.0	0
3.0	307	191	0	2.1	2.2	0
4.0	248	247	0	1.9	1.8	0
5.0	202	293	0.20	1.5	1.5	0.006
7.0	136	354	0.30	1.1	1.0	0.002
16.6	4.91	472	3.78	0.44	0.39	0.012
0.4 mol.L^{-1} LIX 860-I + 0.4 mol.L^{-1} CYANEX 302						
0	503	0	0			
2.0	326	154	0.30	2.9	2.5	0.005
4.0	199	290	0.39	2.1	2.2	0.002
5.3	129	355	0.78	1.8	1.7	0.010
6.4	75.0	395	1.43	1.5	1.1	0.018
7.5	40.9	421	2.16	1.0	0.77	0.022
23.2	0.06	453	52.3	0.08	0.07	0.10

Table F-2. Influence of the strip concentration on the flux of nickel(II)

Time (h)	Ni(II) concentration Feed ($mg.L^{-1}$)	Ni(II) concentration Strip ($mg.L^{-1}$)	Flux Ni(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Ni(II) Strip ($g.m^{-2}.h^{-1}$)
1.5 mol.L^{-1} sulfuric acid				
0	490	0.07		
2.1	462	116	0.10	0.14
3.0	443	162	0.15	0.12
4.0	425	205	0.14	0.11
5.0	407	249	0.13	0.11
6.0	385	293	0.17	0.11
7.0	370	336	0.11	0.11
3 mol.L^{-1} sulfuric acid				
0	468	0		
1.1	455	35.5	0.09	0.09
2.0	440	68.7	0.12	0.08
3.0	424	106	0.12	0.09
4.0	411	148	0.09	0.10
5.0	395	178	0.12	0.08
6.0	388	211	0.05	0.08
7.0	376	232	0.09	0.05

Table F-3. Influence of the carrier concentration on the flux of nickel(II)

Time (h)	Ni(II) concentration Feed ($mg.L^{-1}$)	Ni(II) concentration Strip ($mg.L^{-1}$)	Flux Ni(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Ni(II) Strip ($g.m^{-2}.h^{-1}$)
0.2 mol.L^{-1} LIX 860-I + 0.2 mol.L^{-1} CYANEX 302				
0	466	0		
2.0	455	54.4	0.04	0.07
3.0	451	86.9	0.03	0.08
4.0	443	103	0.07	0.04
5.0	425	135	0.13	0.08
7.0	404	177	0.08	0.05
8.0	393	182	0.08	0.01
0.4 mol.L^{-1} LIX 860-I + 0.4 mol.L^{-1} CYANEX 302				
0	490	0.07		
2.1	462	116	0.10	0.14
3.0	443	160	0.15	0.12
4.0	425	201	0.14	0.10
5.0	407	242	0.13	0.10
6.0	385	281	0.17	0.10
7.0	370	319	0.11	0.09
0.6 mol.L^{-1} LIX 860-I + 0.6 mol.L^{-1} CYANEX 302				
0	465	0		
1.0	455	63.2	0.08	0.16
2.0	432	156	0.17	0.23
3.0	409	222	0.17	0.17
4.0	392	292	0.13	0.18
5.0	358	370	0.26	0.20
6.0	331	413	0.20	0.11
7.0	315	453	0.12	0.10
8.0	307	496	0.06	0.11
0.8 mol.L^{-1} LIX 860-I + 0.8 mol.L^{-1} CYANEX 302				
0	467	0.32		
1.0	455	67.3	0.09	0.17
2.0	438	117	0.12	0.12
3.0	419	173	0.14	0.14
4.0	405	226	0.11	0.13
5.0	384	275	0.16	0.12
6.2	365	335	0.12	0.13
7.0	349	374	0.14	0.12

Annex G

General formulation and technical use of different types of nickel(II) baths

Table G-1. General formulation of nickel(II) baths

Ni(II) (mol.L^{-1})	Cl^- (mol.L^{-1})	SO_4^{2-} (mol.L^{-1})	BO_3^{3-} (mol.L^{-1})	$H_2NSO_3^-$ (mol.L^{-1})	pH	Temperature (°C)
General formulation						
Watt's nickel bath						
1.0-1.2	0.3-0.4	1.0-1.2	0.5-0.7		4.0-4.5	50
Nickel sulphamate bath						
1.4-1.9	0.1-0.2		0.5-0.7	2.3-3.4	3.5-4.5	55
Electroless nickel bath						
0.1		0.1			6-7	80-90

Additives:

Watt's bath: NaCl, saccharine, aromatic sulphonic acids and surfactants.

Sulphamate bath: additives like Watt's bath

Electroless nickel bath: sodium citrate, ammonium sulfate, sodium hypophosphite, 2,4-dihydroxybenzoic acid

Technical uses:

Watt's bath: increased hardness, corrosion resistance and wear resistance, improved appearance (brightness)

Sulphamate bath: coating with lower internal stress as compared to the Watt's bath, thick coating, high plating speed

Electroless nickel bath: constant coating thickness

Annex H

Data of SLM experiments on real effluent streams

Table H-1. Experimental runs with real effluent streams

Effluent	Time (h)	Ni(II) concentration Feed ($mg.L^{-1}$)	Ni(II) concentration Strip ($mg.L^{-1}$)	Flux Ni(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Ni(II) Strip ($g.m^{-2}.h^{-1}$)
Synthetic solution	0	495	0		
	1.0	52.6	425	0.31	0.30
	1.5	2.96	503	0.071	0.11
	2.0	0.171	516	0.004	0.018
	2.5	0.079	516	0	0
Watt's bath	0	496	0		
	0.5	319	161	0.25	0.23
	1.0	218	277	0.15	0.17
	1.5	129	382	0.13	0.15
	2.0	45.7	452	0.12	0.10
	2.5	10.8	499	0.050	0.070
	3.0	2.02	515	0.012	0.021
	3.5	0.763	519	0.002	0.007
	4.0	0.466	516	0	0
	4.5	0.356	518	0	0
Sulphamate bath	0	496	0		
	0.5	303	198	0.28	0.28
	1.0	184	343	0.17	0.21
	1.5	66.1	443	0.17	0.14
	2.0	11.7	518	0.078	0.11
	2.5	0.414	531	0.016	0.017
	3.0	0.362	525	0	0
	3.5	0.304	524	0	0
	4.0	0.154	522	0	0
Electroless nickel bath	0	492	0		
	0.5	319	176	0.25	0.25
	1.0	266	245	0.074	0.10
	1.5	217	288	0.070	0.061
	2.0	176	329	0.059	0.058
	2.5	158	355	0.027	0.037
	3.0	134	377	0.034	0.031
	4.0	97.3	410	0.026	0.024
	5.0	77.4	435	0.014	0.018
	6.0	58.9	445	0.013	0.007
	8.0	37.8	469	0.008	0.009
	9.0	29.9	470	0.006	0.001
	10.0	21.3	474	0.006	0.002
	11.5	18.2	470	0.001	0

Table H-2. Investigation of the stability of the liquid membrane containing 0.4 mol.L^{-1} LIX 860-I and 0.4 mol.L^{-1} CYANEX 302

Time (h)	Ni(II) concentration Strip (mg.L^{-1})	Flux Ni(II) Strip (g.m^{-2}.h^{-1})
2.0	52.31	
3.3	198	0.21
116	3.23×10^3	0.048
212	8.21×10^3	0.091
307	11.8×10^3	0.066
501	19.4×10^3	0.070
837	24.7×10^3	0.028
837	5.19×10^3	
854	5.67×10^3	0.052
1044	16.1×10^3	0.096
1044	3.36×10^3	
1107	7.38×10^3	0.11
1275	12.5×10^3	0.054
1515	17.4×10^3	0.036
2193	26.5×10^3	0.024
2620	27.4×10^3	0.004

Annex I

Data of SLM and PIM experiments

Table I-1. Fluxes of copper(II) obtained with LIX 860-I as extractant in SLM (flat membrane)

Time (h)	Cu(II) concentration Feed ($mg.L^{-1}$)	Cu(II) concentration Strip ($mg.L^{-1}$)	Flux Cu(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Cu(II) Strip ($g.m^{-2}.h^{-1}$)
0	458	0		
1	454	5.40	0.67	0.95
2	433	20.9	3.8	2.7
5	376	87.7	3.4	3.9
6	357	112	3.2	4.2
7	343	139	2.5	4.8
8	330	153	2.2	2.4
24	122	326	2.3	1.9

Table I-2. Influence of the carrier concentration on the copper(II) flux

Time (h)	Cu(II) concentration Feed ($mg.L^{-1}$)	Cu(II) concentration Strip ($mg.L^{-1}$)	Flux Cu(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Cu(II) Strip ($g.m^{-2}.h^{-1}$)
50/30/20 PVC/LIX 860-I/TBEP				
0	93.7	0		
7.0	90.2	0.72	0.09	0.02
23.0	84.3	2.70	0.06	0.02
27.5	83.8	3.20	0.02	0.02
31.0	83.6	3.80	0.01	0.03
46.8	80.4	7.90	0.04	0.05
50.3	79.1	8.50	0.07	0.03
40/40/20 PVC/LIX 860-I/TBEP				
0	97.9	0		
4.0	93.1	0.33	0.21	0.01
7.5	92.1	1.10	0.05	0.04
23.5	84.3	7.90	0.09	0.07
28.0	81.4	10.2	0.11	0.09
31.5	78.6	12.0	0.14	0.09
47.5	72.3	19.6	0.07	0.08
52.0	71.3	21.1	0.04	0.06
30/50/20 PVC/LIX 860-I/TBEP				
0	100	0		
3.5	99.6	3.30	0.04	0.17
7.0	87.1	8.43	0.63	0.26
23.0	65.7	31.9	0.23	0.26
27.5	58.5	36.6	0.28	0.18
31.0	55.2	39.7	0.17	0.16
46.8	42.2	54.0	0.14	0.16
50.3	41.1	56.7	0.06	0.14

Table I-3. Influence of the plasticizer concentration on the copper(II) flux

Time (h)	Cu(II) concentration Feed ($mg.L^{-1}$)	Cu(II) concentration Strip ($mg.L^{-1}$)	Flux Cu(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Cu(II) Strip ($g.m^{-2}.h^{-1}$)
50/40/10 PVC/LIX 860-I/TBEP				
0	97.5	0		
7.3	97.4	0	0	0
23.3	96.6	0.22	0.009	0.002
27.8	95.9	0.38	0.03	0.006
31.3	96.0	0.51	0	0.007
47.3	96.2	1.40	0	0.010
51.8	97.0	1.60	0	0.008
40/40/20 PVC/LIX 860-I/TBEP				
0	97.9	0		
4.0	93.1	0.33	0.21	0.01
7.5	92.1	1.10	0.05	0.04
23.5	84.3	7.90	0.09	0.07
28.0	81.4	10.2	0.11	0.09
31.5	78.6	12.0	0.14	0.09
47.5	72.3	19.6	0.07	0.08
52.0	71.3	21.1	0.04	0.06
30/40/30 PVC/LIX 860-I/TBEP				
0	97.1	0		
3.5	93.3	0.32	0.19	0.02
7.3	87.9	1.20	0.25	0.04
23.3	75.1	4.60	0.14	0.04
27.8	71.9	5.40	0.12	0.03
47.3	65.0	12.6	0.06	0.06
51.8	64.2	14.1	0.03	0.06

Table I-4. Influence of the total mass of a PIM membrane on the copper(II) flux

Time (h)	Cu(II) concentration Feed ($mg.L^{-1}$)	Cu(II) concentration Strip ($mg.L^{-1}$)	Flux Cu(II) Feed ($g.m^{-2}.h^{-1}$)	Flux Cu(II) Strip ($g.m^{-2}.h^{-1}$)
800 mg				
0	96.9	0		
3.5	94.7	0.05	0.11	0.003
7.0	93.5	0.26	0.06	0.01
23.3	89.2	3.70	0.05	0.04
27.3	84.6	5.20	0.20	0.07
31.3	81.4	7.60	0.14	0.11
47.3	75.2	13.0	0.07	0.06
600 mg				
0	97.9	0		
4.0	93.1	0.33	0.21	0.01
7.5	92.1	1.10	0.05	0.04
23.5	84.3	7.90	0.09	0.07
28.0	81.4	10.2	0.11	0.09
31.5	78.6	12.0	0.14	0.09
47.5	72.3	19.6	0.07	0.08
52.0	71.3	21.1	0.04	0.06
500 mg				
0	98.0	0		
4.0	97.0	2.90	0.04	0.13
8.0	95.9	4.40	0.05	0.07
24.0	86.6	12.9	0.10	0.09
28.0	85.4	15.0	0.05	0.09
32.0	83.5	16.5	0.08	0.07
48.0	78.2	22.8	0.06	0.07
400 mg				
0	97.5	0		
4.0	96.0	1.30	0.07	0.06
7.8	93.0	3.20	0.14	0.09
23.8	83.2	15.1	0.11	0.13
27.8	80.3	18.1	0.13	0.13
31.8	77.2	20.5	0.14	0.11
47.8	68.5	30.8	0.10	0.11